1156

PB 210 651

Tyco Laboratories, Inc.
Bear Hill
Waltham, Massachusetts 02154

DEVELOPMENT OF THE CATALYTIC CHAMBER PROCESS

Final Report

Contract No. CPA 70-59

by

A. Gruber
A. Walitt

23 April 1970 – 22 October 1970

Prepared for

Office of Air Programs Environmental Protection Agency
411 W. Chapel Hill Street
Durham, North Carolina 27701

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

155

EC

142 A

BIBLIOGRAPHIC DATA SHEET

1. Report No. APTD-1156

2.

3. Recipient's Accession No. PB-210 651

4. Title and Subtitle

Development of the Catalytic Chamber Process

5. Report Date October 1970

6.

7. Author(s) A. Gruber and A. Walitt

8. Performing Organization Rept. No.

9. Performing Organization Name and Address

Tyco Laboratories, Inc.
Bear Hill
Waltham, Massachusetts 02154

10. Project/Task/Work Unit No.

11. Contract/Grant No. CPA 70-59

12. Sponsoring Organization Name and Address

ENVIRONMENTAL PROTECTION AGENCY
Office of Air Programs
411 West Chapel Hill Street
Durham, North Carolina 27701

13. Type of Report & Period Covered Final

14.

15. Supplementary Notes

16. Abstracts

The objective was to: (1) confirm the technical feasibility of the Catalytic Chamber Process, and (2) obtain preliminary engineering design data necessary for process scale-up. A laboratory-scale investigation was made of the separate process stages and of an integrated 10 SCFM unit called the "miniplant." Three major modifications of the original Lead Chamber Process were investigated: (1) the sulfur dioxide oxidation and the nitric oxide oxidation are performed in separate stages, thus avoiding the need for large reactor volumes to complete the very slow NO oxidation; (2) a high temperature scrubber is used which permits the absorption of the sulfuric acid and oxides of nitrogen but not water, which would dilute the acid; and (3) a catalytic stripper is used to simultaneously remove the oxides of nitrogen from the scrubbing acid and oxidize them to nitrogen dioxide. The following results were obtained: (1) the SO_2 reactor achieved 84-94% conversion of SO_2 to SO_3 at a residence time of 20-22 sec, and inlet SO_2 concentration of 3200-3950 ppm, 290-324 F, and atmospheric pressure; (2) the high temperature scrubber achieved 65% and 45% removal of the NO_x in the inlet gas using 8.5 ft and 5 ft of 3/8-in. Intalox saddles, respectively. The column diameter was 4 in. and the inlet NO_x concentration was ~7000 ppm; (3) the catalytic stripper achieved 95% denitration of the inlet acid. The stripper gas contained 0.39% NO and 0.75% NO_2. The inlet acid concentration was 0.38% wt nitrosylsulfuric acid in 80% sulfuric acid and the stripping temperature was 280-310 F; (4) new NO_x vapor pressure data were obtained for nitrose solutions containing up to 95% H_2SO_4 and at a temperature of 350 F. These new data agree well with earlier data.

17. Key Words and Document Analysis. 17a. Descriptors

Air pollution control equipment
Feasibility
Catalysis
Chambers
Processing
Design criteria
Sulfur dioxide
Oxidation
Nitrogen dioxide
Nitrogen oxides
Sulfuric acid
Nitric acid
Nitrogen oxide (NO)
Sulfur trioxide
Temperature
Scrubbers
Column packings
Vapor pressure

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group 13B

18. Availability Statement

Unlimited

i

19. Security Class (This Report) UNCLASSIFIED

20. Security Class (This Page UNCLASSIFIED

21. No. of Pages 157

22. Price $6.00 / $.95

FORM NTIS-35 (REV. 3-72)

USCOMM-DC 14952-P72

Tyco Laboratories, Inc.
Bear Hill
Waltham, Massachusetts 02154

DEVELOPMENT OF THE CATALYTIC CHAMBER PROCESS

Final Report

Contract No. CPA 70-59

by

A. Gruber

A. Walitt

23 April 1970 – 22 October 1970

Details of illustrations in
this document may be better
studied on microfiche

Prepared for

Office of Air Programs Environmental Protection Agency
411 W. Chapel Hill Street
Durham, North Carolina 27701

Table of Contents

Section Page

SUMMARY 1

I. INTRODUCTION 3

- A. Background 3
- B. The Tyco Catalytic Chamber Process 3
- C. Previous Work 9
- D. Goals of the Contract 10

II. CATALYTIC STRIPPER - CATALYST SELECTION 11

- A. Prior Work 13
- B. Candidate Catalysts 13
- C. Qualitative Screening 14

III. CATALYTIC STRIPPER - ACTIVATED CHARCOAL EVALUATION 19

- A. Batch Tests 19
- B. Continuous Column Experiments (1-In. Column) 21
- C. Continuous Column Experiments (2-In. Column) 27
- D. Summary of Results of Charcoal Evaluation 53

IV. HIGH TEMPERATURE SCRUBBER - LABORATORY EVALUATION 55

- A. Background 55
- B. Equipment Design 55
- C. Operating Conditions 55
- D. Analytical Techniques 58
- E. Experimental Results 58
- F. Summary of Results of High Temperature Scrubber Evaluation 64

V. VAPOR PRESSURE OF NITROGEN OXIDES OVER $HNSO_5/H_2SO_4$ SOLUTIONS 65

- A. Literature Search 65
- B. Laboratory Work at Tyco 69
- C. Interpretation of Tyco Results 79

Table of Contents (continued)

Section Page

VI. LABORATORY SCALE MINIPLANT - MODIFICATION AND EXPERIMENTATION 81

A. Goals of Miniplant Operation 81

B. Miniplant Modification 82

C. Analytical Instrumentation and Sampling Procedures 87

D. Experimental Results 88

VII. ACKNOWLEDGEMENTS 131

VIII. REFERENCES 133

APPENDIX I: PROCESS ECONOMICS

APPENDIX II: MINIPLANT DATA SHEET

APPENDIX III: MINIPLANT EXPERIMENTAL PROCEDURES

APPENDIX IV: MINIPLANT DATA SHEET

List of Illustrations

Figure No. Page No.

1. Catalytic chamber process 4
2. High temperature scrubber 6
3. Catalytic stripper 8
4. Program schedule 11
5. Apparatus for qualitative catalyst evaluation 15
6. Apparatus for continuous, quantitative testing of catalysts 22
7. Continuous stripper experiment 28
8. 2-inch continuous column for catalyst evaluation 29
9. Laboratory apparatus for continuous evaluation of stripper catalyst 31
10. Continuous laboratory stripper test: Experiment 1-A 33
11. Continuous laboratory stripper test: Experiment 1-B 34
12. Continuous stripper experiment: Experiment 1-C 36
13. Continuous stripper test: Experiment 1-D 37
14. Denitration of recycled acid: Experiment 1-E 39
15. Denitration of recycled acid: Experiment 1-F 40
16. Column optimization: Experiment 1-G, air flow rate variation 42
17. Column optimization: Experiment 1-H, air flow rate variation 43
18. Column optimization: Experiment 1-I, air flow rate variation 44
19. Co-current flow: Experiment 1-J 45
20. Countercurrent column operation: Experiment 1-K 47
21. Denitration using reagent grade acid in nitrose: Experiment 1-L 49
22. Stripper blank - saddle packing: Experiment 2-A 53
23. Laboratory scale high temperature absorption column 56

List of Illustrations (Cont)

Figure No. Page No.

24. Laboratory apparatus for continuous evaluation of high temperature scrubber 57

25. Nitrogen oxide partial pressure, nitrosylsulfuric acid concentration dependence 67

26. Nitrogen oxide partial pressure, temperature dependence 68

27. Nitrogen oxide partial pressure, sulfuric acid concentration dependence 70

28. N_2O_3 vapor pressure analysis apparatus 71

29. Total vapor pressure nitrose solutions containing 0.1M $HNSO_5$ 75

30. Nitrogen oxide partial pressures over nitrose solutions containing 0.1M $HNSO_5$ 76

31. Nitrogen oxide partial pressure over nitrose solutions; concentration dependence - experimental values 77

32. Miniplant flowsheet 83

33. Miniplant showing SO_2 reactor and NO oxidizer 84

34. Miniplant showing stripper and scrubber columns 86

35. Miniplant analytical instrumentation 89

36. Gas sampling and analysis system 90

37. Miniplant scrubber evaluation wet feed: NO_x only 102

38. McCabe-Thiele analysis of high temperature scrubber 108

39. Scrubbing efficiency of packed column; experimental and extrapolated values used to determine HTU 113

40. Experimental operating lines – scrubber design 116

41. Scrubber/stripper operating in miniplant - Data from Table XVII 119

42. Scrubber/stripper operation in miniplant - data from Table XVIII 120

43. Scrubber/stripper operation in miniplant - data from Table XIX 121

44. Scrubber/stripper operation in miniplant - data from Table XXIII 122

45. Modified catalytic stripper - recycle concept 128

List of Tables

Table Page

I Results of Qualitative Screening Tests 17

II Batch Experiments – Characterization of Charcoal Catalyst 20

III Continuous Column Tests – 1-In. Column 24

IV Batch Tests With Activated Charcoal 26

V Comparative Analyses of Acid Samples 51

VI High Temperature Scrubber Experimental Results 250°F Steady State Operation 2-in. × 40-in. Column Packed with 1/4-in. Procelain Intalox Saddles 59

VII High Temperature Scrubber Experimental Results 250°F Steady State Operation 2-in. × 40-in. Column Packed with 1/4-in. Porcelain Intalox Saddles 60

VIII Operation of Scrubber Using Pure NO as Feed Steady State Operation 63

IX Tyco Sample Compositions 72

X Tyco Vapor Pressure Data for 80.08 wt % H_2SO_4 73

XI Tyco Vapor Pressure Data for 84.04 wt % H_2SO_4 73

XII Tyco Vapor Pressure Data for 90.16 wt % H_2SO_4 74

XIII Tyco Vapor Pressure Data for 95.0 wt % H_2SO_4 74

XIV Miniplant Experimentation – Reactor Evaluation 94

XV Miniplant Reactor Experiments 96

XVI Miniplant Evaluation of Scrubber 97

XVII Miniplant Scrubber Evaluation 99

XVIII Miniplant Scrubber Evaluation 100

XIX Miniplant Scrubber Evaluation 101

XX Residence Volumes and Times in Miniplant Reactor and Analytical System 104

XXI Miniplant Reactor Experiments 106

XXII Equilibrium Data 109

XXIII Miniplant Scrubber Evaluation 111

XXIV Extrapolated Scrubbing Efficiencies Based on Experimental Column Tests 112

List of Tables (continued)

Tables Page

XXV Calculation of Mass Transfer Coefficients (K_ga) and Height of Transfer Unit (HTU) 117

XXVI Design and Conditions for Operation of Laboratory and Miniplant Catalytic Stripper 123

XXVII Miniplant Stripper Verification Experiment No. 1 126

XXVIII Miniplant Stripper Verification Experiment No. 2 127

XXIX Estimated Major Equipment Cost I-1

XXX Estimated Capital Cost Summary I-2

XXXI Annual Operating Costs I-3

XXXII Miniplant Startup Procedure III-1

XXXIII-XXXVI Miniplant Data Sheets IV-1-IV-4

from page 3

SUMMARY

The objective ~~of this contract~~ was to: ~~(1)~~ confirm the technical feasibility of the Catalytic Chamber Process, and ~~(2)~~ obtain preliminary engineering design data necessary for process scale-up. ~~The contract work consisted of~~ a laboratory-scale investigation was made of the separate process stages and of an integrated 10 SCFM unit, called the "miniplant."

The Catalytic Chamber Process, which is based on the Lead Chamber Process for sulfur acid manufacture, accomplishes the removal of sulfur dioxide by oxidation with nitrogen dioxide followed by adsorption of the resulting sulfuric acid and the oxides of nitrogen in a recycle stream of sulfuric acid. The nitrogen oxides are recovered by catalytic stripping of the sulfuric acid; the net nitrogen dioxide recovered by the process is converted to nitric acid; and the bulk of the nitrogen dioxide is recycled for further sulfur dioxide oxidation. Three major modifications ~~of the original Lead Chamber Process~~ were investigated ~~during this contract~~: ~~(1)~~ the sulfur dioxide oxidation and the nitric oxide oxidation were ~~are~~ performed in separate stages, thus avoiding the need for large reactor volumes to complete the very slow NO oxidation; ~~(2)~~ a high temperature scrubber was ~~is~~ used, which permits the absorption of the sulfuric acid and oxides of nitrogen but not water, which would dilute the acid; and ~~(3)~~ a catalytic stripper was ~~is~~ used to simultaneously remove the oxides of nitrogen from the scrubbing acid and oxidize them to nitrogen dioxide.

The following results were obtained:

1. The SO_2 reactor achieved 84-94% conversion of SO_2 to SO_3 at a residence time of 20-22 sec, and inlet SO_2 concentration of 3200-3950 ppm, 290-324°F, and atmospheric pressure.

2. The high temperature scrubber achieved 65% and 45% removal of the NO_x in the inlet gas using 8.5 ft and 5 ft of 3/8-in. Intalox saddles, respectively.* The column diameter was 4 in. and the inlet NO_x concentration was ~7000 ppm.

---

*These data were extrapolated to show that 97% of the NO_x could be removed in 30 ft of packed bed.

3. The catalytic stripper achieved 95% denitration of the inlet acid. The stripper exit gas contained 0.39% NO and 0.75% NO_2. The inlet acid concentration was 0.38% wt nitrosylsulfuric acid in 80% sulfuric acid and the stripping temperature was 280-310°F.

4. New NO_x vapor pressure data were obtained for nitrose solutions containing up to 95% H_2SO_4 and at a temperature of 350°F. These new data agree well with the earlier data of Berl and Saenger.[5]

The results of the contract work indicate that the following additional work should be performed:

a. A parametric study of process variables using the 10 SCFM miniplant,

b. Investigation and demonstration of a process control system,

c. Preliminary design of a 2000 SCFM pilot plant.

I. INTRODUCTION

A. Background

The Catalytic Chamber Process is aimed at solving one of our most pressing air pollution problems: the emission of enormous quantities of sulfur dioxide and nitrogen oxides into the atmosphere from the stacks of power plants burning fossil fuels. This problem has become so severe that at the present time the amount of sulfur dioxide emitted into the atmosphere in the United States is equivalent to more sulfuric acid than is produced for industrial purposes.* In addition to the serious sulfur dioxide problem, there has been a growing awareness of the detrimental effect of nitrogen oxides on man and his surroundings. It has also been established that NO_2 is a key participant in the photochemical oxidation of unburned hydrocarbons from automotive exhaust to form smog.

The Catalytic Chamber Process features the oxidation of SO_2 to SO_3 through the use of nitrogen dioxide as a homogenous, gas-phase, reactive catalyst in a manner similar to the old Lead Chamber Process. The initial work performed under contract to NAPCA was undertaken to determine the ability of NO_2 to oxidize the dilute sulfur dioxide present in flue gas. This work has led to the present Catalytic Chamber Process concept.

to p. 1

B. The Tyco Catalytic Chamber Process

The most recent conceptualization of the Tyco process for the removal of SO_2 and NO_x from the power plant stack gas has been named the Catalytic Chamber Process because of the novel manner in which the oxides of nitrogen are recovered for reuse as the SO_2 oxidant. In this process, the oxides of nitrogen are removed from the scrubbing solution by contacting the nitrose with air in a fixed bed of activated charcoal. The charcoal catalytically oxidizes the NO values in the nitrose to NO_2 which, being only slightly soluble in sulfuric acid, is spontaneously evolved from solution into the gas phase. The Catalytic Chamber Process is composed of three major process units: (1) the SO_2 reactor, (2) the high temperature scrubber, and (3) the catalytic stripper (see Fig. 1). The raw flue gas is cleaned of most of

---

*In 1966, for example, U.S. sulfuric acid production was about 22 million tons as compared to 44 million tons of equivalent acid from all stationary sources and about 20 million tons from power plants alone.[1, 2]

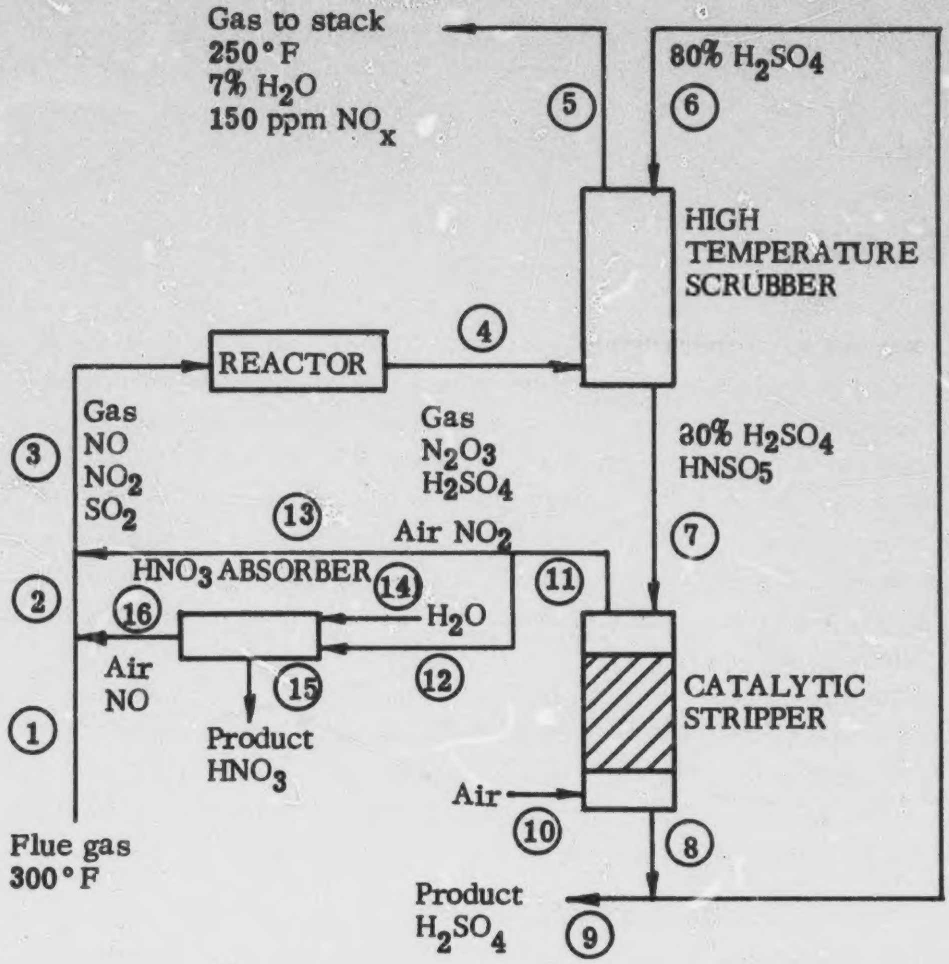

Gas to stack
250 °F
7% H2O
150 ppm NOx
⑤
80% H2SO4
⑥
HIGH TEMPERATURE SCRUBBER
REACTOR
④
Gas
NO
NO2
SO2
③
Gas
N2O3
H2SO4
30% H2SO4
HNSO5
⑦
⑬
Air NO2
HNO3 ABSORBER
⑭
⑪
②
⑯
H2O
Air
NO
⑮
⑫
CATALYTIC STRIPPER
①
Product
HNO3
Air
⑩
⑧
Flue gas
300 °F
Product
H2SO4
⑨

Fig. 1. Catalytic chamber process

the fly ash and is contacted with a stream of recycle NO_2. The NO_2 oxidizes the SO_2 to SO_3. The SO_3 and H_2O in the flue gas react to form $H_2SO_4(g)$. The reacted gases are passed through a sulfuric acid scrubber to remove the newly-formed acid and the oxides of nitrogen. The clean, wet stack gas is vented to the atmosphere at about 250°F and is easily dissipated. The nitrogen oxide-bearing sulfuric acid (nitrose) from the scrubber is passed countercurrent to air across activated charcoal catalyst. The nitrose is catalytically oxidized to NO_2 with air, and the NO_2 exits the stripper with the air stream. Part of the NO_2 rich gas stream from the stripper, equivalent to the net NO_x recovered by the process, is used to produce nitric acid in a conventional nitric acid plant. The bulk of the NO_2 rich gas stream is recycled to the SO_2 reactor for further SO_2 oxidation. Sulfuric acid, equivalent to the SO_2 recovered by the process, is removed as product from the denitrated acid leaving the stripper.

1. Reactor

The reactor accomplishes the oxidation of SO_2 to SO_3 and the hydrolysis of SO_3 to H_2SO_4:

$$SO_2 + NO_2 \rightarrow SO_3 + NO$$

$$SO_3 + H_2O(g) \rightarrow H_2SO_4(g)$$

Important features of this stage include: (1) maintaining a sufficiently high temperature to avoid condensation of the acid mist in the reactor, and (2) providing twice the stoichiometric amount of NO_2 so that the full reacted gas will contain an equimolar amount of NO and NO_2, thus enabling recovery of the oxides of nitrogen. The reactor residence time is long enough to permit high yield oxidation of the SO_2, but not long enough to permit appreciable oxidation of the nitric oxide. The NO is oxidized in the catalytic stripper (see below), and the NO_2 is recycled to the reactor to oxidize more SO_2.

2. Scrubber

The high temperature scrubber removes the sulfuric acid mist and the oxides of nitrogen present in the reactor exit gas (see Fig. 2). The oxides of nitrogen must be present in equimolar quantities. NO or NO_2 alone are insoluble in sulfuric acid; but together, as N_2O_3, they react with sulfuric acid to form nitrosylsulfuric acid, which is soluble in sulfuric acid:

$$NO_2 + NO + 2H_2SO_4 \rightarrow 2HNSO_5 + H_2O$$

The scrubber operating temperature is that temperature for which the H_2O vapor pressure of the incoming acid is equal to the partial pressure of water in the incoming gas.

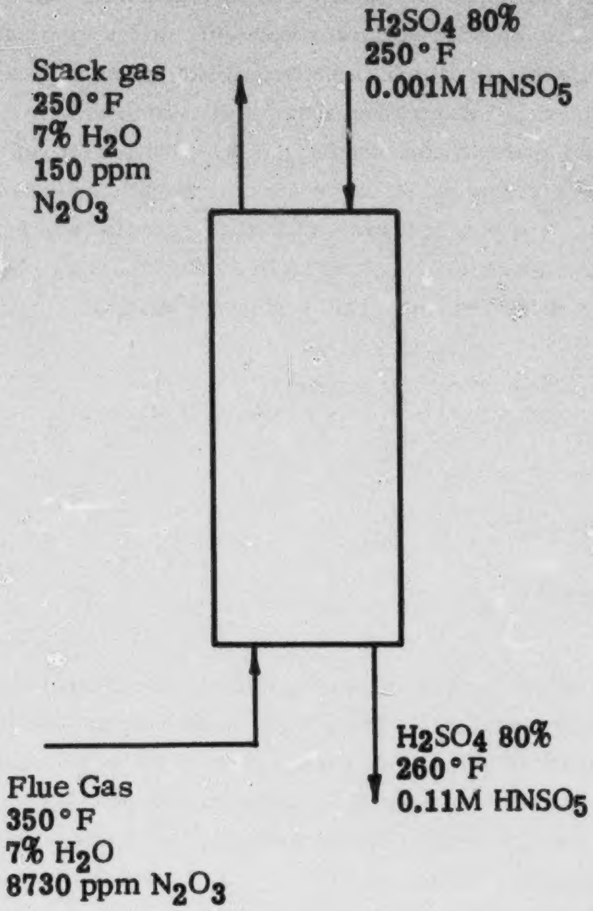

Stack gas
250 °F
7% H_2O
150 ppm
N_2O_3
H_2SO_4 80%
250 °F
0.001M $HNSO_5$
Flue Gas
350 °F
7% H_2O
8730 ppm N_2O_3
H_2SO_4 80%
260 °F
0.11M $HNSO_5$

Fig. 2. High temperature scrubber

Thus, no water is absorbed in the column and the acid leaves the scrubber at the same concentration as it entered. For 80% acid and a gas stream containing 7.3% water, this temperature is 250°F. It should be noted that the Lead Chamber Process uses cold sulfuric acid for scrubbing.

Since the solubility of nitrosylsulfuric acid increases with increasing H_2SO_4 concentration, it may be desirable to operate the scrubber at acid strengths above 80% H_2SO_4, the concentration utilized by the Lead Chamber Process. For the Catalytic Chamber Process, a limitation on the acid concentration is imposed by the sulfuric acid content of the exit gas. As the acid concentration is increased, the operating temperature of the scrubber must be increased in order to maintain the water vapor pressure over the entering acid equal to the partial pressure of water in the entering gas. As the scrubber temperature is increased, the sulfuric acid content of the exit gas increases. An acid concentration of about 92%, for example, requires a 400°F scrubber temperature and results in about 2 mm H_2SO_4 in the exit gas. The limitation of the standard Lead Chamber Process in the increasing degree of difficulty of denitrifying higher strength sulfuric acid is overcome in the Catalytic Chamber Process through the use of the catalytic stripper, as discussed in detail below.

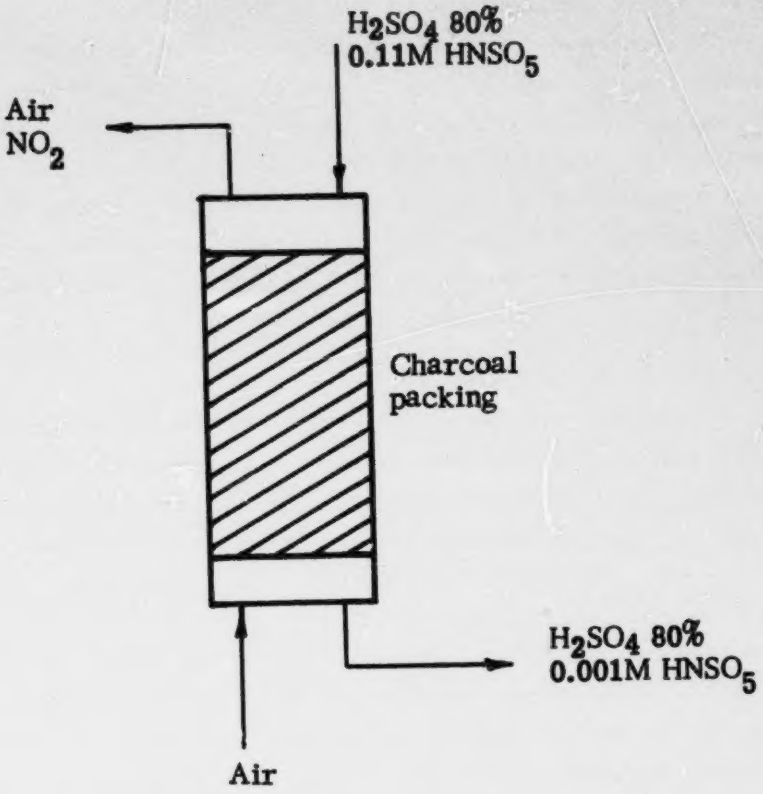
3. Catalytic stripper

In the standard chamber plant, the nitrogen oxides are sufficiently concentrated so that reoxidation can occur simultaneously with sulfur dioxide oxidation even though the reaction rate is quite slow in comparison at the operating temperature used. Nitrogen oxide recovery is effected by the dilution and heating of the nitrose, which causes an increase of the vapor pressure of the oxides that are then swept out of the acid by the high temperature gases from the sulfur burner.

Both heating and diluting are impractical when treating dilute, wet flue gases in the Catalytic Chamber Plant because they involve a requirement for heat beyond that which enters the system with the flue gas. Heat balance calculations on such a system show that the heat penalty would be enormous; as much as 20% of the total heat generated by the power plant would be necessary.

The breakthrough achieved during this research which avoids this heat penalty was the discovery that, by contacting the nitrose with a catalyst such as acitivated charcoal in the presence of oxygen, the oxides of nitrogen are oxidized to nitrogen dioxide in the liquid phase and are recovered quantitatively in a relatively small volume of carrier gas. Fig. 3 shows a schematic diagram of the catalytic stripper that would be used to accomplish the nitrogen oxide recovery.

The exact mechanism of the oxidation reaction has not yet been determined, but the net effect is that the total nitrogen oxide content of the nitrose is converted to the relatively insoluble nitrogen dioxide which is spontaneously evolved from the sulfuric acid. No additional heat is required to drive the reaction to completion; as a matter of fact, the overall process is negligibly exothermic.



H_2SO_4 80%
0.11M $HNSO_5$
Air
NO_2
Charcoal packing
H_2SO_4 80%
0.001M $HNSO_5$
Air

Fig. 3. Catalytic stripper

4. Process economics

Investmentt and operating costs have been estimated by Tyco Laboratories, Inc., and by the Tennessee Valley Authority, as shown below:

	Tyco	TVA
Size	800 MW	500 MW
Flue Gas Flowrate (MM SCFM)	1.44	1.0
NO_x concentration, ppm	600	400, 1200
SO_2 concentration, ppm	3000	3000
NO_2 concentration	30	20, 60
S in coal % wt	3.5	3.5
Investment Cost $MM	11.5	10.7
Annual Operating Cost	3.7	2.4

Refer to Appendix I for a breakdown of the above costs.

The net operating costs are highly dependent on the market price of the product acids. If the nitric acid and sulfuric acid prices are $40/ton and $9.50/ton, respectively, the net operating costs are zero.* If the prices are higher, the Catalytic Chamber Process will produce a return on the investment.

C. Previous Work

The work performed under a prior contract (PH 86-68-75) had several intermediate goals which are worth discussing before going into detail on the current work. This background will clarify the orientation and goals of the current contract.

1. Initial evaluation of the Lead Chamber Process

The earliest work at Tyco concerning this technology was the evaluation of the Lead Chamber Process for direct application as a flue gas cleanup technique. These experiments involved kinetic studies of the SO_2 oxidation and NO reoxidation reactions, as well as preliminary analysis of the NO_x scrubbing process.

It was concluded from this work that the Lead Chamber Process could not be used for flue gas cleanup without modification. The oxidation of SO_2 by NO_2 could be accomplished under the dilute conditions present in the flue gas but the simultaneous NO oxidation was impossible. In addition, scrubbing with cold sulfuric acid removed all the water from the flue gas and diluted the acid. Heat was needed for the recovery of the oxides of nitrogen from the scrubbing acid and the reconcentration of the acid – almost 40% more heat than was provided by the flue gas. Subsequent work concentrated on finding ways of avoiding the disadvantages of the basic Lead Chamber Process.

---

*Prices are based on 100% acid strengths.

2. Modification of the Lead Chamber Process

Three major modifications of the original process were conceived: (1) NO reoxidation separate from the SO_2 oxidation, (2) high temperature NO_x scrubbing to avoid dilution of the recycle acid, and (3) catalytic oxidation of the oxides of nitrogen in the liquid phase to enable NO_2 recovery and recycle without additional heat (see Part B of this section). Each of the three process stages (reactor, scrubber, and stripper) was evaluated by laboratory-scale experimentation.* Then, a 10 SCFM laboratory-scale pilot plant (miniplant) was designed, built, and operated in order to evaluate the new process stages on an integrated basis.

D. Goals of the Contract

The goals of Contract CPA 70-59 were: (1) to continue the individual bench-scale evaluation of the reactor, the scrubber, and the stripper, and (2) to operate the miniplant.

More specifically, the work was to include the following tasks:

1. Selection of a catalyst to be used in the catalytic stripper,
2. Operation of a laboratory-scale catalytic stripper to determine operating characteristics,
3. Operation of a laboratory-scale, high-temperature scrubber to verify the high-temperature removal of oxides of nitrogen from the reacted flue gas without the dilution of the acid,
4. Determination of N_2O_3 vapor pressure data for nitrose solutions at higher concentrations than were currently available in the literature,
5. Modification of the miniplant according to the results of 1-4 above,
6. Operation of the miniplant on a continuous basis to obtain process data.

A program schedule of the time spend on each of the six tasks is shown in Fig. 4.

---

*Refer to the final report of Contract No. PH 86-68-75 for more details.

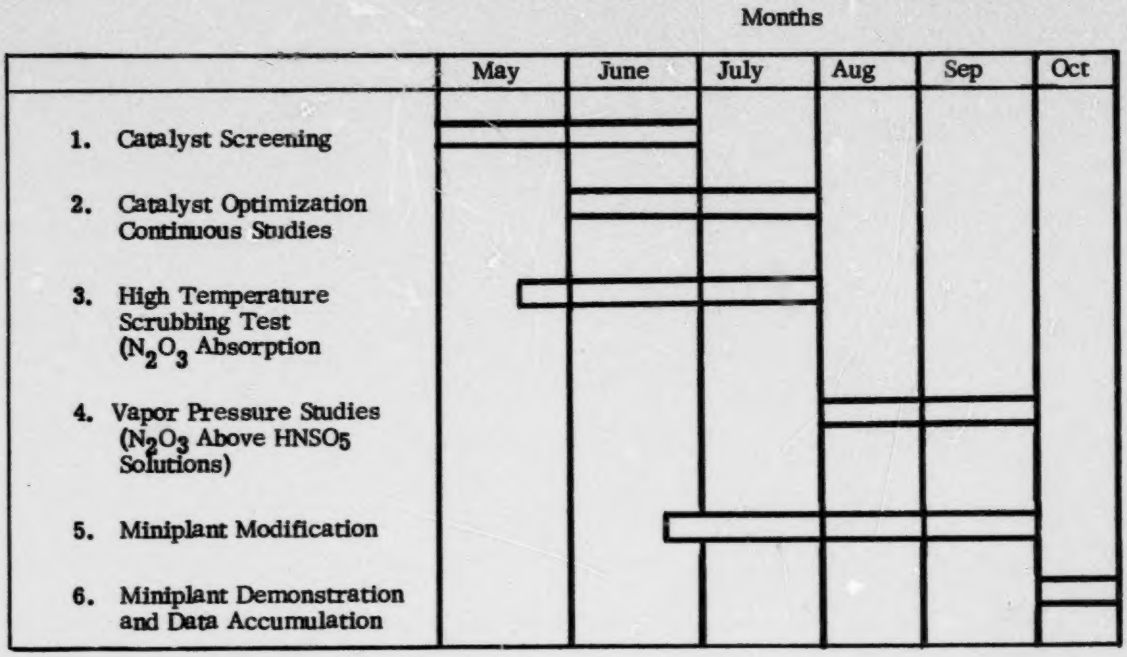


Fig. 4. Program schedule

II. CATALYTIC STRIPPER – CATALYST SELECTION

A. Prior Work

It was demonstrated that nitrosylsulfuric acid in sulfuric acid (nitrose) could be denitrated quantitatively by contacting the nitrose with air in the presence of activated charcoal catalyst. The proposed mechanism for the denitration/oxidation reaction is:

$$4\ HNSO_5 + 2\ H_2O + O_2 \xrightarrow[\text{catalyst}]{\text{activated charcoal}} 4\ NO_2 + 4\ H_2SO_4 \qquad (1)$$

The NO_x in the effluent gas from the stripper was almost completely in the form of NO_2; the difficult gas phase NO oxidation was thus avoided.

Activated charcoal was an effective catalyst for the above reaction but appeared to have stability problems. There was evidence that the NO_2 had reacted with the carbon to form small quantities of carbon dioxide and nitrous oxide (N_2O). In addition, the carbon bed eventually became plugged with very fine pieces of carbon, which were assumed to result from the physical breakdown of the activated carbon particles. Thus, it was decided to look at other potential catalysts during Contract CPA 70-59 to see if there was a material better suited to the task.

B. Candidate Catalysts

A screening program was set up to determine if materials other than activated charcoal could be used to catalyze Reaction (1). The screening program consisted of two phases: (1) a literature study in which candidate materials were chosen on the basis of physical properties, and (2) an experimental study of the ability of the candidate materials to catalyze the oxidation of nitrosylsulfuric acid.

The candidate catalysts had to be insoluble in hot (250 to 400°F) sulfuric acid solutions (75 to 90%) containing about 1% nitrosylsulfuric acid and resistant to oxidation at temperatures between 70 and 400°F. Thus, the oxides of nickel, cobalt, and iron and many of the pure metal catalysts were eliminated from consideration. Refractory metals and their carbides, nitrides, borides, etc., and activated carbon were chosen as candidate catalysts.

Preceding page blank

1. Carbides

The carbides were considered prime candidates because of their general stability and the similarity between the carbide and activated carbon structures. Boron carbide, silicon carbide, tungsten carbide, nickel carbide, titanium carbide, and molybdenum carbide were considered. Boron carbide was considered the best candidate because it is commercially available and is relatively inexpensive, even though the surface area is approximately 1 m^2/g as compared to 500-1000 m^2/g for the activated carbon. Molybdenum carbide was considered the worst candidate because molybdenum compounds are apparently somewhat soluble in sulfuric acid.

2. Silicides, nitrides, and selenides

This candidate list included the silicides and nitrides of boron, silicon, and tungsten. The selenides were eliminated because of their toxic nature.

3. Tungsten bronzes

These materials were chosen because of their acid stability. They have been placed low on the priority list because they are somewhat hard to obtain (they are not widely commercially available).

4. Other materials

Consideration was given to other materials, including pure metals such as tungsten, titanium, platinum, rhenium, and tantalum. They were not considered prime candidates because most of them are extremely expensive and are known to be easily poisoned. There was also the possibility of using some of the refractory compounds with a trace of metal (platinum, rhenium, etc.) as a promoter. Such mixed systems are of considerable interest but will receive secondary consideration because of the greater difficulty in obtaining them.

C. Qualitative Screening

After a list of candidate materials had been determined, several were tested qualitatively by a simple experimental procedure designed to evaluate their gross ability to catalyze the liquid-phase oxidation of nitrosylsulfuric acid at high temperatures. The apparatus used (see Fig. 5) consisted of a large test tube fitted with a fritted glass sparging tube and a gas outlet which led to an infrared analytic cell. A quantity of catalyst material was placed in the tube and 25 ml of nitrosylsulfuric acid (0.7%), in 80% sulfuric acid at 210°F, was added to the catalyst. The air bleed was inserted, and the test tube was placed in an oil bath, also at 210°F. The air was passed through the system for 10 to 15 min, after which the acid was cooled and analyzed for nitrosylsulfuric acid content using potassium permanganate to determine oxidizable nitrogen oxide species. Details of this analytical procedure can be found in

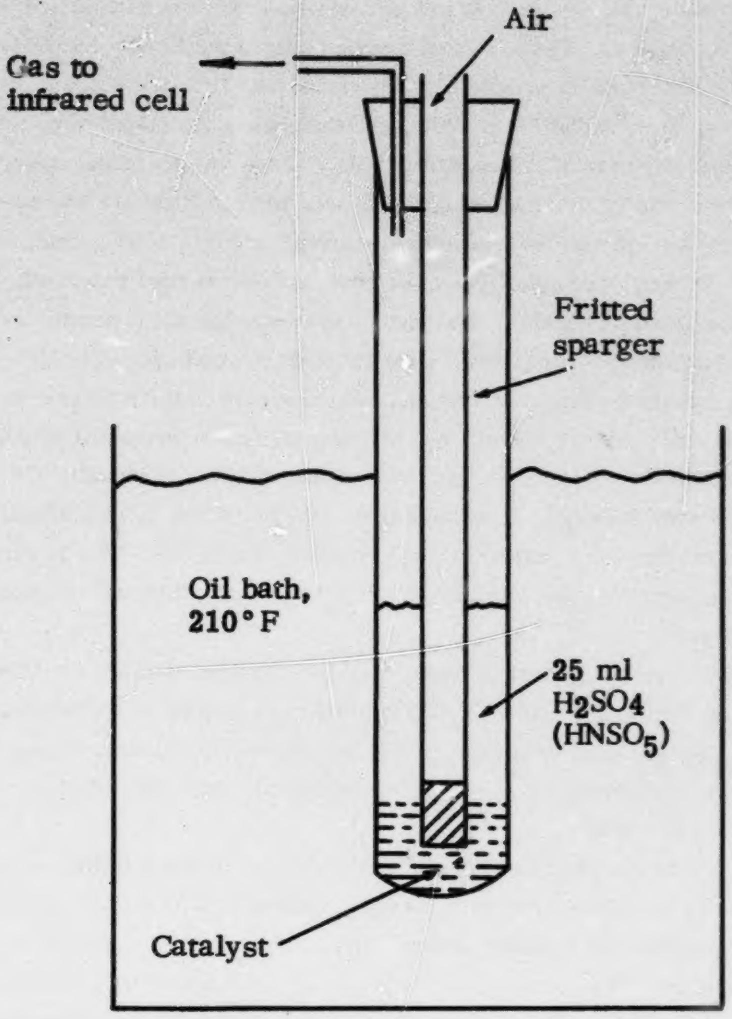

Air
Gas to infrared cell
Fritted sparger
Oil bath, 210°F
25 ml H_2SO_4 ($HNSO_5$)
Catalyst

Fig. 5. Apparatus for qualitative catalyst evaluation

Appendix II. An infrared spectrum of the effluent gas was taken during the run. The spectrum and acid content were compared with control runs on crushed saddles and activated carbon. The results of a series of these tests are shown in Table I.

As was expected, the saddles had no catalytic effect on the acid and no significant denitration was observed. The activated carbon reduced the $HNSO_5$ level of the acid, but not as much as was expected. A sample of the charcoal was first treated with the $HNSO_5$ solution, washed in water, dried at 250°F for 2 hr, and then run in the standard test. The acid was reduced to a concentration of only 0.075% $HNSO_5$, which was more in keeping with previous experience. Apparently, the original charcoal was wet and little air was adsorbed on the surface, and the air sparger was not efficient enough to allow good contact in the three-phase system: air, catalyst, and acid. When the charcoal was washed and dried, more air was adsorbed on the charcoal surface, thus providing oxygen for the denitration reaction.

It was interesting to note that, when the charcoal was used directly as-received, the resulting acid contained many fines (as had been observed in the earlier contract work). However, when the charcoal was washed in acid, then washed in water and dried, subsequent acid treatment showed no evidence of the fine charcoal particles. Obviously, the initial contact with the acid causes some reaction, breaking off the fine particles; but additional treatment with acid does not affect the charcoal and it will be physically stable. This is very significant in light of previous observations that the fines tend to plug the charcoal columns after initial treatment with acid.

Materials such as silicon carbide, tungsten silicide, titanium carbide, and platinum black showed no evidence of catalytic activity and can probably be eliminated from further consideration. Others such as nickel, nickel boride, nickel carbide, nickel with platinum, tungsten boride, and titanium boride can be eliminated, since they showed a tendency to react with acid or dissolve in it.

There remains a group of materials which shows some activity, although none appear to be as active as the activated carbon. Boron carbide, silicon nitride, boron nitride, tungsten carbide, and vanadium carbide are in this latter category. Boron carbide is of doubtful usefulness, since it may likely contain a relatively large amount of free carbon, and it is this carbon that might well be causing the denitration oxidation reaction. This is reinforced by the observation that the purer carbide obtained from Cerac Company had less tendency to catalyze the reaction (see tests 4 and 4).

Although there was no material that was as good as activated charcoal, this did not rule out replacement of the carbon with one of the other materials such as tungsten carbide or silicon nitride. The next step in ascertaining the utility of these potential replacements was to test them in a more quantitative fashion in a continuous column containing material balance data. A column was arranged so that acid and gas could be fed countercurrently at known rates and the effluent materials collected and analyzed.

Table I. Results of Qualitative Screening Tests (Temperature: 200 to 210° F; Original Acid Concentration: 0.720% $HNSO_5$)

Catalyst	Time of Test, min	Final Acid Concentration, % $HNSO_5$	Other Interactions With Acid*
1. Crushed saddles	10	0.718	None
	20	0.720	
	15	0.714	
2. Activated carbon (Witco grade 256)	10	0.450	Evidence of N_2O
	20	0.401	
	15	0.412	
	15	0.425	
	10†	0.076	
3. Silicon carbide (Carborundum no. 6-RA)	15	0.704	None
	10	0.688	
4. Boron carbide (Norton)	15	0.550	Some N_2O
	15‡	0.413	
	10	0.569	
5. Boron carbide§ (Cerac)	10§	0.637	Some N_2O
6. Nickel	10	0.681	Some reaction
7. Nickel boride	10	0.427	Some reaction
8. Nickel carbide	10	0.463	Reaction
9. Nickel with platinum	10	0.686	Slight reaction
10. Silicon nitride	15	0.590	None
	15	0.497	
	10	0.586	
11. Tungsten boride	15	0.428	Reaction
	10	0.354	
12. Boron nitride	15	0.566	None
	10	0.653	
13. Tungsten silicide	15	0.669	None
14. Tungsten carbide	15	0.603	None
	10	0.576	
	10	0.505	
	10	0.542	
15. Titanium carbide	15	0.670	None
16. Vanadium carbide	15	0.594	None
17. Titanium boride	10	0.292	Some reaction
18. Platinum black	10	0.647	None

---

*This refers to either solubility of the catalyst in the acid or a tendency for the system to oxidize the catalyst.

†This carbon sample was prewashed in $HNSO_5$ solution, washed in H_2O, and dried.

‡Additional B_4C was added after 5 min and after 10 min

§This B_4C was of higher purity than the Norton material.

There would be little difficulty in column testing the granular charcoal or boron carbide, but the other promising materials mentioned were far more difficult to test in the continuous apparatus since they were available only in extremely fine powders (325-mesh or finer). In order to test them in a column, it would have been necessary to find a way to make porous pellets from the powders. A company that specialized in powder metallurgy techniques was located (Advanced Metallurgy, Inc., of McKeesport, Pennsylvania), and they felt that they could make macroporous pellets from the fine powders; but their price was quite high and it was decided to more fully evaluate the charcoal before pellets were made.

As later results will show, the carbon performance was good enough that it was not considered necessary to go back and more fully evaluate the other potential catalysts. There are many advantages for using activated carbon, including availability and price, and it was felt that carbon should be used if possible. The work on the other catalyst materials was discontinued at this stage with the conclusion that there are other materials that can be used in the catalytic stripper and if there are any major problems in the future we could return to this work.

III. CATALYTIC STRIPPER - ACTIVATED CHARCOAL EVALUATION

A. Batch Tests

1. Prewashing with $HNSO_5$

The tests in Table I show that the activated charcoal provided about 40% denitration of a 0.72% $HNSO_5$ solution if the carbon was used in the as-received form. If the carbon was first washed in $HNSO_5$ solution and then washed in water and dried, about 90% of the $HNSO_5$ in the solution was removed.

To further evaluate this effect as well as the long term stability and reusability of the carbon, an experiment was set up where the carbon was tested for catalytic activity on a batch basis, then washed, dried, and retested. The carbon used was Witco type 256, 4 × 10 mesh. After each test, the carbon sample was weighed and screened to test for particle breakdown. The batch test procedure was the one described in Section II of this report. As shown in Part A of Table II, the results of these repeated tests indicate that the carbon activity is maintained over a period of six repetitions of the test with no physical or catalytic activity degradation.

It was interesting to note that, although the activated carbon lost a small amount of material in the form of fines the first time it was contacted with nitrosylsulfuric acid, subsequent denitration runs and washings did not produce any further fines. The carbon appears to have stabilized after this first washing.

2. Teflon impregnation of the charcoal

One idea concerning the maintenance of the physical stability of the carbon was to impregnate the carbon particles with TFE Teflon. The charcoal particles were allowed to absorb the Teflon from a liquid dispersion of the polymer after which the excess liquid was drained off and the charcoal particles sintered at 280 °C. It was felt that not only would the Teflon improve the physical stability of the charcoal, but it would improve the diffusion of the oxygen into the pores of the carbon by making the surfaces more hydrophobic.

A sample of carbon was treated in this fashion and tested in the same way as above (water washed and dried between tests). The analysis of the final acid concentration shows that the carbon had lower activity after the Teflon treatment, and after several tests the carbon appeared to maintain a constant level of activity although at a considerably lower level than without the Teflon impregnation (see Part B of Table II). Since the untreated carbon appeared

Table II. Batch Experiments — Characterization of Charcoal Catalyst

	Test		Final Acid Concentration*
A.	Witco carbon type 256 4 × 10 mesh 1250 m^2/g (total surface area) carbon tested with standard test procedure then washed to effluent pH ~ 4.0; dried 2 hr at 120 °C (tests repeated six times)	1	.104
		2	.054
		3	—
		4	—
		5	.061
		6	.064
B.	Same carbon as A with Teflon sintered into structure; test procedure the same as A	1	.375
		2	.542
		3	.541
		4	.550
		5	.568
C.	Witco carbon type 517 20 × 40 mesh 1050 m^2/g (total surface area); standard test — two reruns with no wash or dry treatment between runs	1	.366
		2	.055
		3	.145
D.	Nuchar carbon type C-190-N, very fine (< 325 mesh)	1	.176
E.	Same carbon as C; standard test using N_2 instead of air	1	.247

---

* Inlet acid for all experiments had a concentration of 0.670% $HNSO_5$ by weight.

to be quite stable physically, there seems to be no advantage at this time to continuing this line of experimentation.

3. Evaluation of smaller particle carbon

There was some thought that there was not really enough contact time to allow the oxygen and the acid to diffuse into the fine pore structure of the carbon particles and react there, and that most of the reaction was occurring on the outer surface of the carbon particles. If that were true, an equal volume of a small sized carbon would have a higher outer surface area and the reaction should be accelerated. This concept was evaluated by testing Witco type 517 carbon which had a particle size of 20 × 40 mesh. A sample of this carbon was tested three times without washing between tests.

The results are shown in Part C of Table II with the first test on as-received carbon exhibiting lower activity than the larger size particles (which had a higher total surface area, although a lower outer surface area). Additional tests show improved activity although the third test seems to be going to lower activity. The increase in activity after an initial test has been demonstrated several times for different carbons and suggested that the as-received carbon does not have maximum activity. A washing with acid is necessary to remove adsorbed material from the carbon surface and free it for catalytic activity.

Another test was run with an even finer carbon: Nuchar type C-190-N with a particle size of less than 325 mesh. As shown in Part D of Table II, the results are good but not significantly better than any other carbon.

4. Using nitrogen as the treatment gas

A sample of the Witco 517 carbon was run in the standard batch test and the final acid concentration was considerably lower than the original acid (see Part E of Table II). This result suggests that either the acid is reacting with oxygen adsorbed on the carbon, or the acid is only being thermally stripped. The test results using saddles would tend to deny this latter possibility since considerable stripping did occur. The question then arises as to whether or not the original adsorbed oxygen that is used is ever replaced during the reaction. The test results in Part A of Table II are not completely applicable here as the acid was washed out of the carbon and the particles dried, thus allowing the readsorption of more oxygen. In order to evaluate this concept, the continuous column apparatus was used to get long term activity data on a single bed of carbon.

B. Continuous Column Experiments (1-In. Column)

1. Apparatus and procedure

To obtain long term stability and activity characteristics of the Witco type 256 activated carbon, a continuous column apparatus was constructed using Corning 1-in. conical pipe. As shown in Fig. 3, the apparatus contained a removable section so that the catalyst could be examined or replaced without dismantling the entire apparatus.

The acid was heated in a container above the column and then dripped into the column; the flow being controlled by a stopcock. (This control was difficult to achieve and the flow

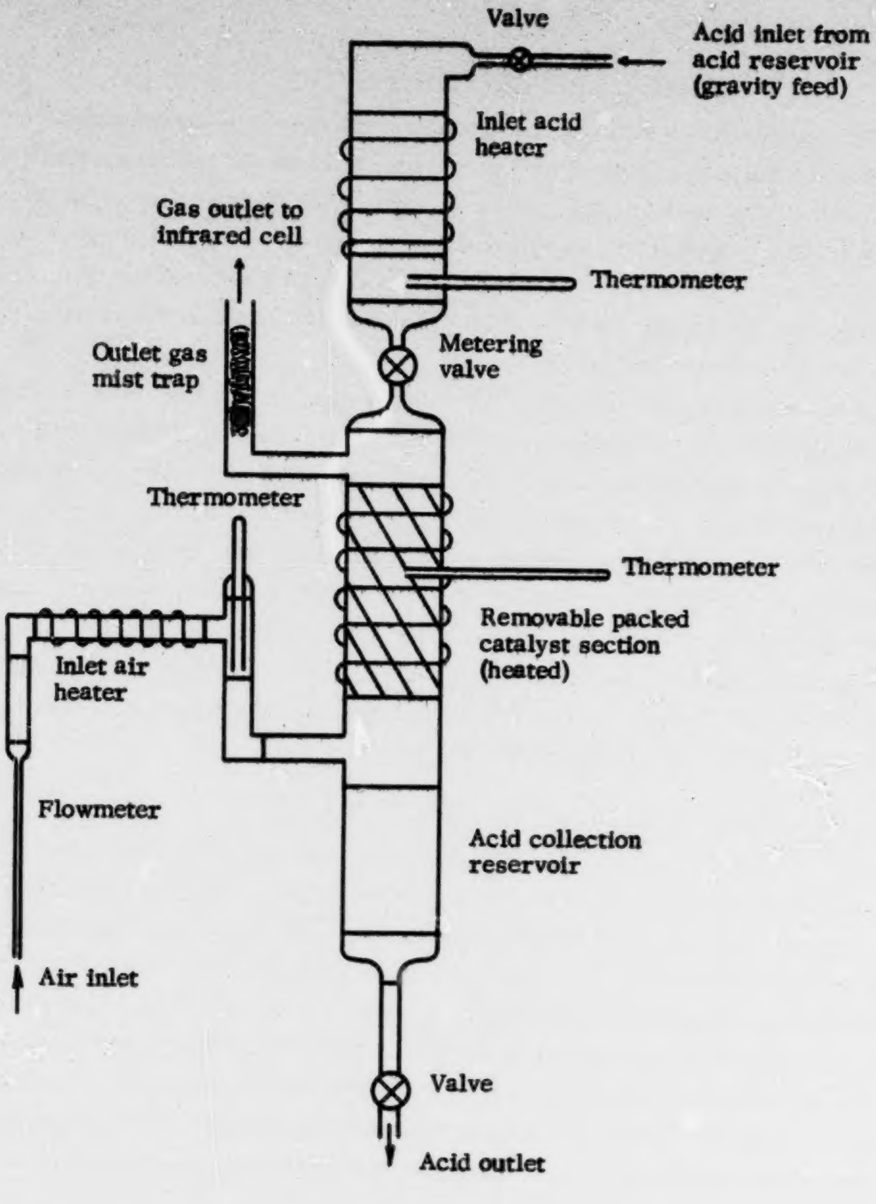

Valve
Acid inlet from acid reservoir (gravity feed)
Inlet acid heater
Gas outlet to infrared cell
Thermometer
Outlet gas mist trap
Metering valve
Thermometer
Thermometer
Removable packed catalyst section (heated)
Inlet air heater
Flowmeter
Acid collection reservoir
Air inlet
Valve
Acid outlet

Fig. 6. Apparatus for continuous, quantitative testing of catalysts

rates were somewhat erratic.) The acid passed through the charcoal bed and was collected in a receiver below the carbon bed. Periodically this receiver was drained and the acid analyzed for $HNSO_5$ using the $KMnO_4$ method (see Appendix II).

An attempt was made to preheat the entering air stream, but the procedure was very inefficient and it was finally decided to feed the air at room temperature. (Since the total heat capacity of the air is small compared to the acid, this had little or no effect on the operating temperature of the column). The exit gas was fed to the infrared batch cell for analysis.

2. Continuous tests

Several tests were run with this column with the results being given in Table III. The column was somewhat difficult to operate in a completely continuous manner since flooding frequently occurred in the charcoal beds due to packing support plates which did not have enough open spaces to allow free drainage. There was no apparent plugging due to catalyst breakdown. The flooding problem was solved in later experimentation as will be described below.

Test A in Table III shows that, after running 89 ml of 0.639% $HNSO_5$ through the column (which contained about 80 g of fresh, washed, and dried carbon, Witco type 256), the acid was denitrated to 0.384% $HNSO_5$, a 40% reduction. A second run, test B, showed that the rate of denitration was dependent upon the acid-gas flow ratios, with denitration being increased when the acid flow was reduced. During this stage, denitration of about 75% was achieved.

The material from test B was run again and the activity of the carbon appeared to go rapidly down to zero with the final effluent acid being almost as concentrated as the input acid. To try to duplicate the wash and dry batch experiments (Table II-A), the column was washed with water followed by a 2-hr period where air was passed through the column at room temperature. Acid was then passed through the column again using countercurrent air feed with the result shown in test D in Table III. The impression that is gained from these results is that the wash water was never really dried out of the column and the low initial acid concentrations merely reflected some dilution of the acid.

Test E was made with the finer Witco type 517 carbon in three beds (in series), but again the carbon appeared to drop in activity. This is shown more clearly in test F (which used a single layer of Witco type 517 carbon) where the activity of the carbon dropped off steadily during the test. Both of these tests were run at room temperature to see if activity was improved at lower operating temperatures. (It should be recalled that the gas phase oxidation of NO to NO_2 takes place at higher rates as the temperature is reduced. These tests were aimed at evaluating the possibility of a gas phase oxidation mechanism. The results did not support such a hypothesis.)

An extended test was run at high temperatures with the Witco type 517 carbon with the results shown as test G in Table III. The temperature was controlled fairly close to 200°F with the acid flow rate varying between 0.5 and 1.0 ml/min. During the 530 min of actual operation, 412 ml of acid was passed through the column with the effluent acid showing a

Table III. Continuous Column Tests — 1-In. Column

Catalyst		Air Flow, cc/min	Temperature, °F	Acid Flow, cc/min	L/G mole/mole	Cumulative Time, min	Output Acid	
							Cumulative Volume, ml	Concentration % $HNSO_5$
A. Witco carbon type 256 4 × 10 mesh fresh carbon (80 g)		115	200	3.0^1	18.5	25	75	
						30	89	0.384
B. Type 256 (dried)		115	140	4.4^1	27.1		25	0.563
		100	220	0.8^1	5.7		100	0.172
C. Type 256 (dried) Material from B		115	175-220	3^1	18.5	10	30	0.356
						45	115	0.621
D. Material from C: water passed through column followed by 2 hr of air drying at R.T. in column		200	200	3.2^1	11.3	10	30	0.018^2
		200	175	2.5^1	8.8		300	0.500
E. Witco type 517 three layers, 1 1/2-2 in. each, 20 × 40 mesh (70 g)		200	R.T.	1^1	3.5		80	0.176
		200	R.T.	1^1	3.5		105	0.523
F. Type 517 single layer ~4 in., dired (25 g)		200	R.T.	3^1	10.6		25	0.238
							55	0.420
							85	0.666
							115	0.640
G. Type 517 three layerc dried 2 hr (120°C);	1	200	70-175	1^3	3.5	90	30^4	0.296
	2		185			120	80	0.209
				r hr hold at 125°F				
	3		185			175	155	0.023
	4		185-210			215	180	0.367
	5		205-220			240	205	0.175
	6		210			270	230	0.191
	7		220			280	255	0.310
	8		175-220			320	280	0.362
	9		100-195			360	305	0.497
	10		175-205			405	350	0.527
	11		175-205			445	375	0.677
	12a		190-205	5^3	17.6	480	385	0.566
	12b		190-205			510	395	—
	12c		~205			530	412	0.859

Notes: 1. Input acid = 0.639% w $HNSO_5$

2. Probably includes some wash water that was not dried out

3. This is in addition to acid needed to soak dry column initially

4. Input acid = 0.661% w $HNSO_5$

steadily decreasing catalyst activity. At the end of this period, the effluent acid was at the same concentration as the incoming acid although the operating conditions were no different from the point at which the column was achieving better than 70% denitration. This type of behavior suggested that the denitration oxidation reaction was dependent on the oxygen adsorbed on the fresh carbon and little or no additional oxygen was being adsorbed during the operation of the column.

3. Theoretical considerations

It would appear from test G above that the denitration reaction continued until a given amount of oxygen present on the carbon had been used up and then the carbon showed no further activity. This type of behavior called for a closer look at what might be occurring during the reaction.

A possible mechanism might include the diffusion of the oxygen through the acid to an adsorption site followed by the adsorption of the oxygen onto the carbon. Simultaneously, the nitrosylsulfuric acid has to diffuse through the acid to the oxygenated active site where the oxidation reaction would take place. Thus it would be one of these three processes that might be the rate limiting step in the overall reaction: (1) oxygen diffusion, (2) oxygen adsorption, and (3) $HNSO_5$ diffusion. It is also possible that it could be the actual oxidation reaction itself that would be the limiting step, but then there should be no variation in denitration rate with time. The behavior pattern observed is also inconsistent with the concept that the diffusion of the $HNSO_5$ to the active site is the rate limiting step. If the mechanism suggested above is correct, then it would appear that it is either the diffusion of the oxygen to the active site or the adsorption of the oxygen at that site that is the limiting step in the reaction.

If it is the adsorption at the active site that limits the overall reaction rate, this could be ascertained by intentionally removing all the oxygen from the charcoal by prolonged exposure to boiling water, drying in nitrogen at temperatures above the proposed operating temperature, cooling in nitrogen to prevent oxygen adsorption, and then attempting to use the so-treated charcoal in a standard batch test. If indeed it is the adsorption rate that limits the reaction, this treatment should render the charcoal virtually inert and a batch test should show no activity.

A series of batch tests was run which sheds some light on the problem. The results on these tests are shown in Table IV. What is strikingly obvious in the results shown in the carbon tests (tests C and D in Table IV) is that within a moderate limit of error all samples were denitrated to the same degree, regardless of prior history. That this should be true even of the sample that was never exposed to air throughout the entire test is quite unusual, but explainable: Exposing the carbon to boiling water limits the degassing to 212 °F, and it is well known that this type of treatment is not effective in removing all the oxygen adsorbed on activated carbons. It would seem that sufficient oxygen remained on the carbon (even after the high temperature drying) to achieve a high level of denitration during the batch test.

Table IV. Batch Tests With Activated Charcoal*

Test	Temperature, °F	Final Acid Concentration, % $HNSO_5$
A. Blank (saddles/air)	250	0.698
B. Blank (saddles/N_2)	250	0.726
C. Carbon (as-received)		
1. air	275	0.192
2. air	265	0.083
3. air	265	0.201
D. Degassed Carbon Contacted with boiling water for 1 hr under nitrogen then dried (260-300 °F) and cooled under nitrogen		
1. Exposed to air 1 hr before test: test run with air	250	0.153
2. Kept under N_2 until test: test run with air	250	0.096
3. Kept under N_2 until test: test run with N_2	250 250	0.163 0.114

---

* All carbon tests on Witco type 256 activated charcoal using stock $HNSO_5$ solution containing 0.740% $HNSO_5$ by weight.

4. Continuous column test - temperature variation

One test was run in the 1-in. column to see the effect of varying the temperature on the denitration capability of the activated charcoal. Three beds of Witco type 256 carbon were set up in series with provision made for determining the acid temperature in the second bed. The acid was again collected in the reservoir at the bottom of the column and sampled at regular intervals. Both the acid and the air were fed to the column at 75 to 80 °F and were heated in the column by heating tapes wrapped around the pipe sections. The column temperature was varied during the experiment.

Fig. 7 is a graphic representation of the history of this experiment. The graph shows the concentration of the effluent acid as a function of the total amount of acid that was passed through the column. The circles indicate the data points taken and are numbered in order while the column temperatures are indicated next to the data points. The air flow was also varied during the experiment, and the flow rates are shown at the bottom of the graph.

At the beginning of this run, about 70% denitration was achieved at a relatively low temperature (point 1 at 145 °F). This activity dropped off sharply and was probably due to loosely adsorbed oxygen and air trapped in the pores of the carbon. Then, after point 3 at 165 °F, the activity increased as the temperature rose to 220 °F at point 6, but dropped off again at points 7 and 8. Apparently the additional oxygen available at the higher temperatures was used up and activity decreased. At this point, the air flow was increased by an order of magnitude and the activity increased again and remained relatively constant from point 9 to point 13 when the air flow was increased again. Again the activity increased although the temperature dropped to 210 °F. From there to the end of the experiment at point 17, the activity of the carbon dropped greatly as the temperature was reduced to 185 °F.

It would appear from this experiment that both temperature and air flow play important parts in the denitration oxidation reaction. When the air flow was increased at constant temperature the activity increased, and when the temperature was increased at constant air flow the activity again increased. These phenomena were evaluated more completely in subsequent experiments.

C. Continuous Column Experiments (2-In. Column)

1. Column redesign

The main problems with the 1-in. column were consistent acid holdup while air was flowing and the difficulty in preheating the acid and feeding it at a controlled rate. These problems were solved by utilizing a 2-in. column constructed in a modular fashion from 2-in. Corning flanged pipe. The packing support plates were redesigned to permit easy flowthrough of the acid, and a simple acid heater was installed which allowed the close control of incoming acid temperature. Acid flow rates were controlled by the use of a variable speed peristaltic pump (Randolph pump, model 250). As shown in Fig. 8, the pump delivered the acid to a heated 1-in. tube, and the acid was fed to the column by overflow through a U-tube arrange-

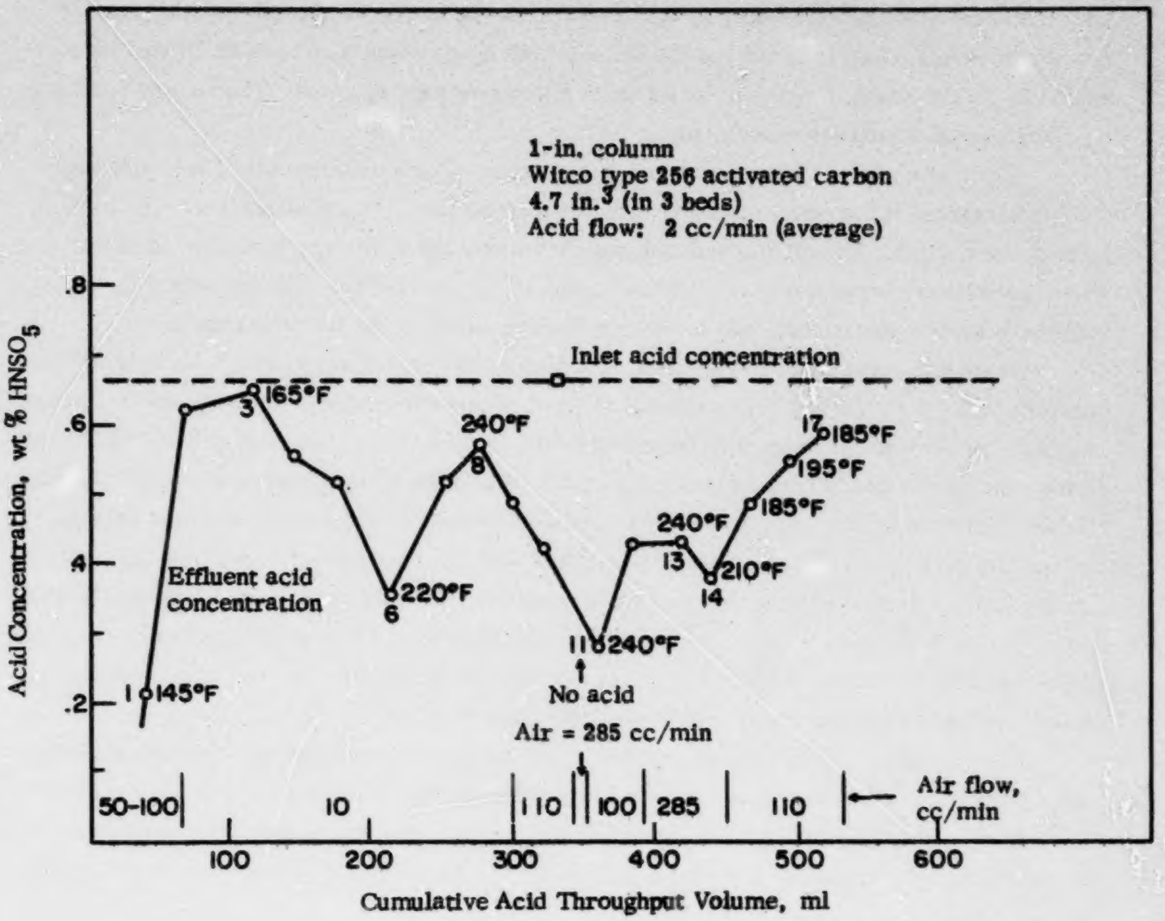


Fig. 7. Continuous stripper experiment

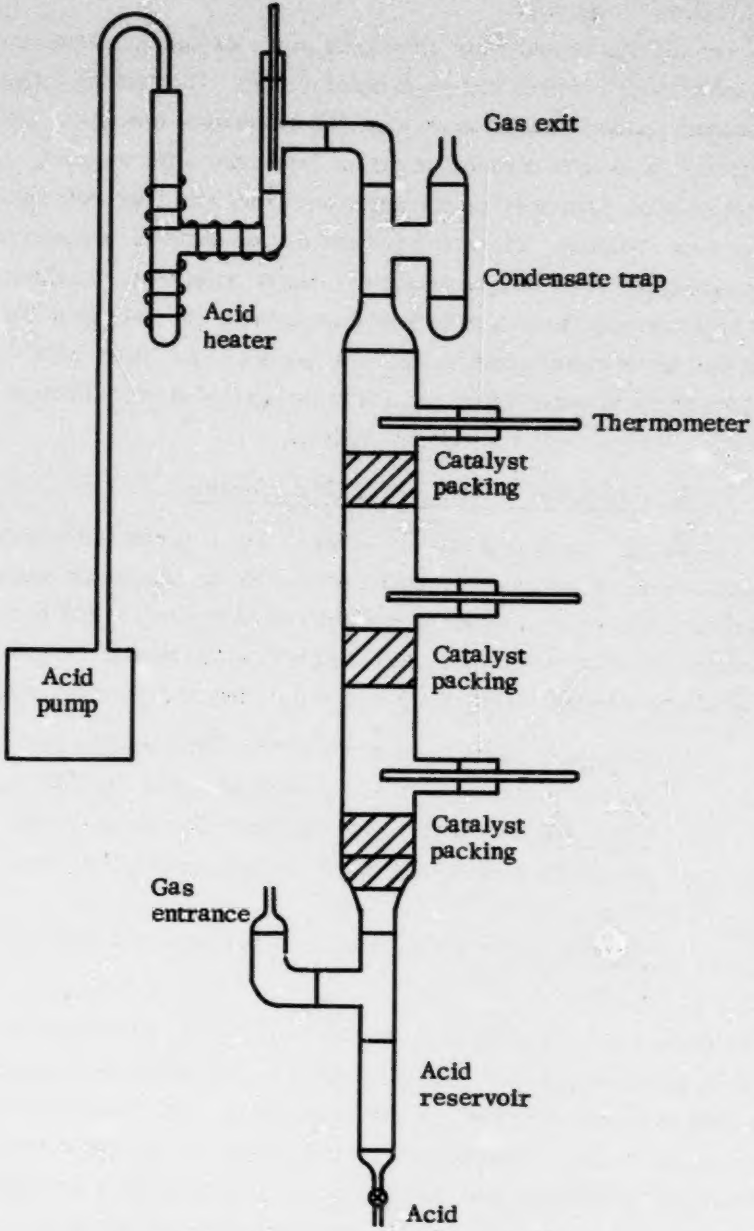

Gas exit
Condensate trap
Acid
heater
Thermometer
Catalyst
packing
Catalyst
packing
Acid
pump
Catalyst
packing
Gas
entrance
Acid
reservoir
Acid
exit

Fig. 8. 2-inch continuous column for catalyst evaluation ment. The U-tube system provided a gas seal at the top of the column. A photo of the apparatus is shown in Fig. 9.

The column was composed of three beds in series and thermometer wells were installed so that the temperature of each bed could be monitored. The packing support plates were made of Teflon and were slotted so that more than 60% of the area was open. Small glass rods were placed vertically in some of the slots to act as downcomers for the acid. A large empty section was placed at the bottom of the column to act as an acid reservoir which could be periodically drained for sampling. The entire packed section could be removed from the column without disturbing the basic setup so that the catalyst could be easily changed or examined.

An initial attempt was made to heat the incoming air, but again this proved inefficient and the air was fed at room temperature. The gas outlet was fitted with a small amount of glass wool for stopping water vapor and a trap was provided for collection of the water. The gas outlet was fed to the infrared cell for analysis.

2. Continuous column testing (2-in. column)

During a period of several weeks, many experiments were performed in the 2-in. column. Since the column contained a removable section which housed the catalyst bed, it was possible to run several experiments with one bed, remove that bed section and replace it with another, and then return to the first bed without disturbing the packing in either bed. Three beds were evaluated during this phase of the work and were set up as follows:

Column 1: Three beds of Witco type 256 activated charcoal in series containing a total depth of 10 in. of catalyst and about 30 cu in. of material

Column 2: Identical in size and configuration to column 1 except that the beds were packed with 1/4-in. ceramic saddles to act as a blank for the charcoal test

Column 3: One bed of Witco type 256 activated carbon packed to a depth of 22 in.

The results of the testing in each column are given graphically by showing the $HNSO_5$ concentration of the effluent acid as a function of the amount of acid passed through the column and comparing this concentration with that of the input acid. The plots show cumulative acid throughput as the abscissa with the total figures giving the amount of acid passed through each column since the column was first packed. Thus the graphs show not only the results of each specific experiment, but also the long term stability and activity of the catalyst bed.

3. Testing with column 1

Throughout the testing with this column, the acid flow rate was maintained at about 10 ml/min while the air flow rate was varied depending on the goals of the individual experiment. The temperatures of the three beds were continuously monitored, and it was found to be difficult to maintain the same temperature in all three catalyst beds. The tempera-

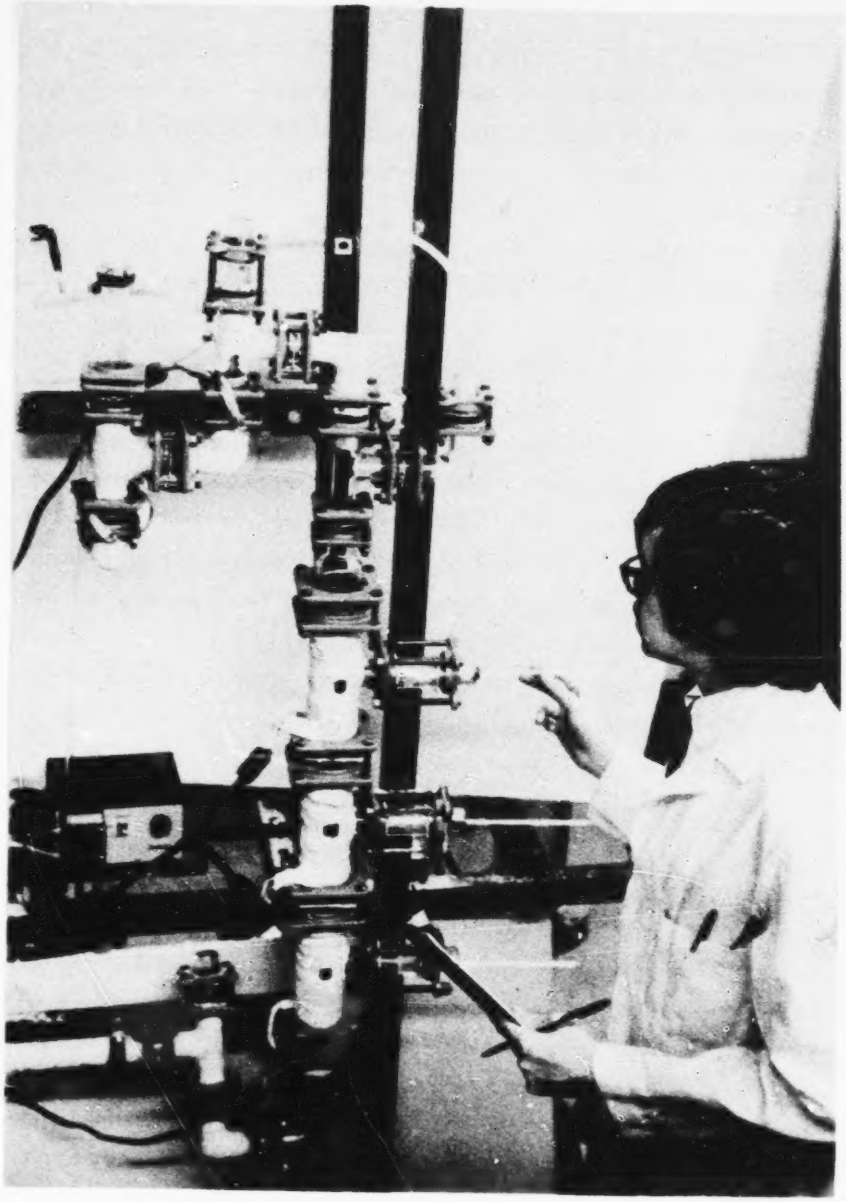


Fig. 9. Laboratory apparatus for continuous evaluation of stripper catalyst

ture that will be used to describe the operating condition of the column will be the highest temperature which consistently occurred in the middle section. The bottom bed was usually within 10 °F while the top section was often 20 °F cooler. Acid samples were taken and analyzed for $HNSO_5$ content every 15 min.

Experiment 1-A: denitration at 200 °F — In this experiment, the temperature was maintained fairly constant at 190 to 205 °F as can be seen from the data in Fig. 10. Although the catalyst showed good activity for the first 1500 ml of acid throughput, the level of denitration dropped off sharply after that, as shown by the jump in output acid concentration after point 12 on the graph.

The first 22 points suggest a behavior pattern that was described in Section B-3 above. The catalyst was providing oxygen that had been adsorbed prior to the test and when that oxygen was used up, the reaction virtually stopped. At point 23, the acid was stopped and air was forced through the column (at a rate in excess of 1000 cc/min). After this, the low flow of 300 cc/min of air was resumed and the activity appeared to have increased. It would seem that the period of air flushing restored some of the carbon's activity after which the activity again decreases toward the plateau level of points 15 through 22. At point 26, the air flow was doubled to 600 cc/min, and the catalyst activity again increased noticeably. After point 27, the air was pulsed through the column: 1 min at 300 cc/min and 1 min at such a rate that the acid would not flow through the carbon beds. This was maintained for about 30 min through data points 28 and 29.

This experiment apparently shows that after the carbon's initial quantity of adsorbed oxygen is used up, it becomes largely inactive. However, if the air supply is greatly increased, some of the original activity can be restored.

Experiment 1-B: denitration at 250 °F — After point 29, the column was shut down and cooled overnight with experimentation being resumed the next day at the same operating conditions (low air flow) as during most of test 1-A. As can be seen in Fig. 11, the effluent acid showed the same level of activity as when the air had been pulsed but quickly resumed the low plateau level of the previous day (points 15 through 22). After point 33, the air flow was increased to 800 cc/min and again the denitration increased. It was clear that a higher air flow rate was needed to maintain acceptable denitration rates at the 200 °F temperature level.

At this point (data point 35), the column temperature was increased and immediately the denitration rate increased. Although there was an inexplicable jump at points 40, 41, and 42, the activity of the catalyst appeared to level off at about 70% denitration when the column temperature leveled off near 250 °F.

This experiment suggests that higher temperatures are necessary to achieve an acceptable level of denitration, but whether this is due to increased diffusion rates or because of the capability to provide larger required activation energies for adsorption was not certain at this time. In any case, it appears that 70% or better denitration is possible at this temperature and at this acid/catalyst contact time.

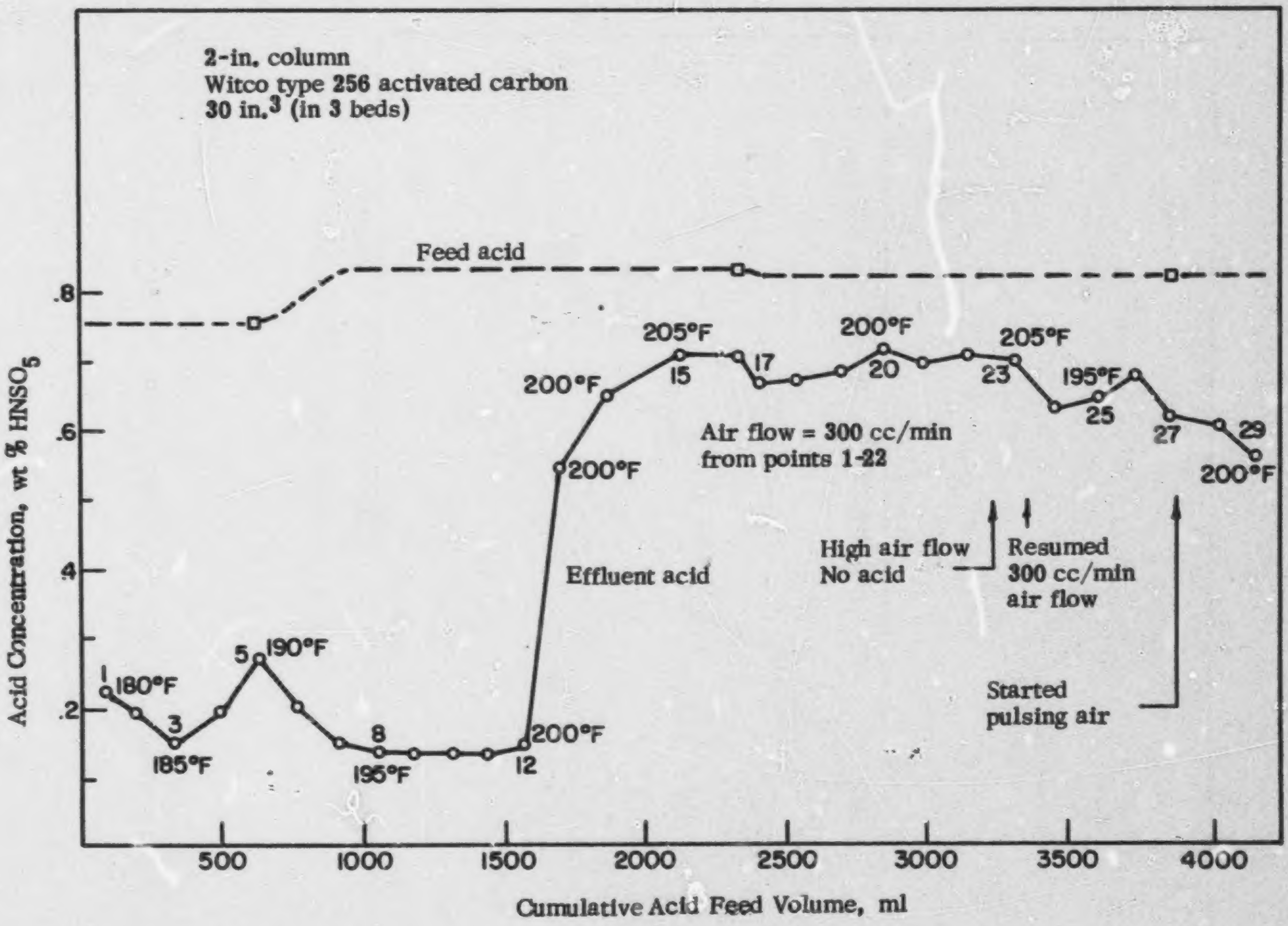


Fig. 10. Continuous laboratory stripper test: Experiment 1-A

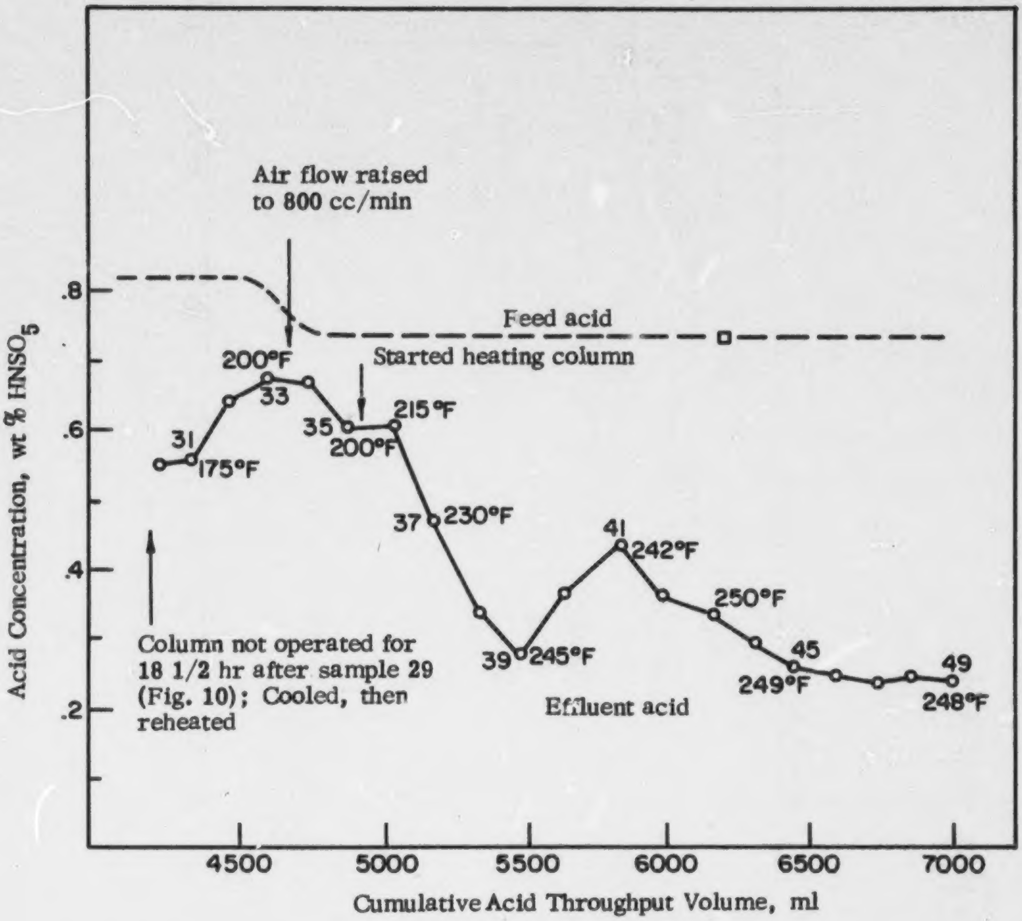


Fig. 11. Continuous laboratory stripper test: Experiment 1-B

Experiment 1-C: extended period denitration — Test 1-B was terminated before it could be ascertained that we were not just utilizing additional oxygen that might be available at higher temperatures, but were really in a steady state situation. Therefore, test 1-C was run after a 3-day shutdown and is shown by data points 50 through 102 in Fig. 12. This run which covered 13 hr and almost 7 ℓ of acid makes it clear that steady state can be achieved at 50 to 60% denitration at 250 to 260 °F and the existing contact time. In test 1-C, the entire operation was started at room temperature and data points taken as the column was slowly heated to its steady state maximum of about 260 °F. Again the catalyst showed poor activity at low temperatures but increased significantly as 260 °F was approached. It is interesting to note the difference in the slopes in test 1-B (points 36 through 39) and 1-C (points 52 through 62) which appear to be directly proportional to the heating rate in each experiment. (One additional point should be noted before the discussion continues: the low concentration of the input acid in the 11,000 to 12,500 ml total acid period.) The practice was to mix the acid in 2 ℓ quantities and take a sample from the hot feed acid midway during the 2-ℓ feed period. These analysis points are shown by the boxed data points on the inlet acid concentration line. The sample taken during the period in question exhibited bubbles which were not seen during any of the other sample analyses and might have been due to a wet or dirty sample flask. It is felt that this inlet level appears lower than it really was and the fact that the outlet acid showed no corresponding change in concentration tends to verify this feeling.

Experiment 1-D: denitration at 290 °F — Having achieved greatly improved continuous denitration levels at 260 °F, it was decided to evaluate still higher temperatures. Test 1-D (Fig. 13) was therefore run at a steady state operating temperature of 290 °F with the resulting improved denitration level shown between data points 108 and 119. Under these conditions, the stripper caused about 75% denitration of the nitrose.

These higher temperatures were chosen in order to determine the effect of temperature variation on the denitration capability of the charcoal and to try to obtain sufficient information to understand the mechanism whereby the charcoal effects denitration of the nitrose. The 290 °F used in experiment 1-D was higher than originally recommended for the recycle temperature of the 80% acid loop, but this temperature range is certainly worth investigation since variations in input flue gas conditions and changes in acid concentration might well require higher operating temperatures. It is clear from these first few experiments that denitration of nitrose by contact with activated charcoal is temperature dependent with distinct advantages possible with high temperature operation of the stripper.

The experiments tend to indicate that the carbon is behaving in a catalytic fashion and appears to be stable for extended periods of time. One might reasonably ask if the denitration is simply due to the vapor pressure of the N_2O_3 above the nitrosylsulfuric acid and has nothing to do with catalytic activity. Calculations show that, if 0.8% $HNSO_5$ solution were flowing at 10 ml/min and air were flowing at 600 cc/min and the acid was denitrated to 0.2% $HNSO_5$, the partial pressure of N_2O_3 in the gas stream would be 11.4 mm Hg. Using the data of Berl and

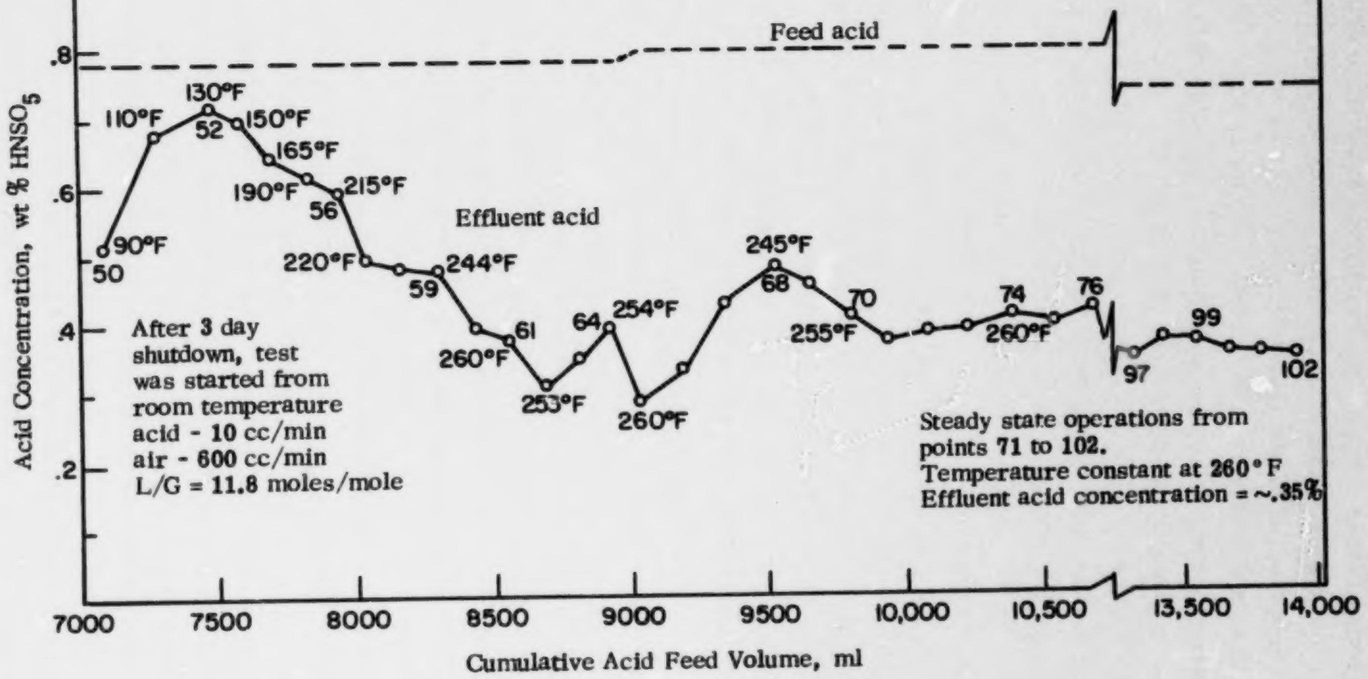


Fig. 12. Continuous stripper experiment: Experiment 1-C

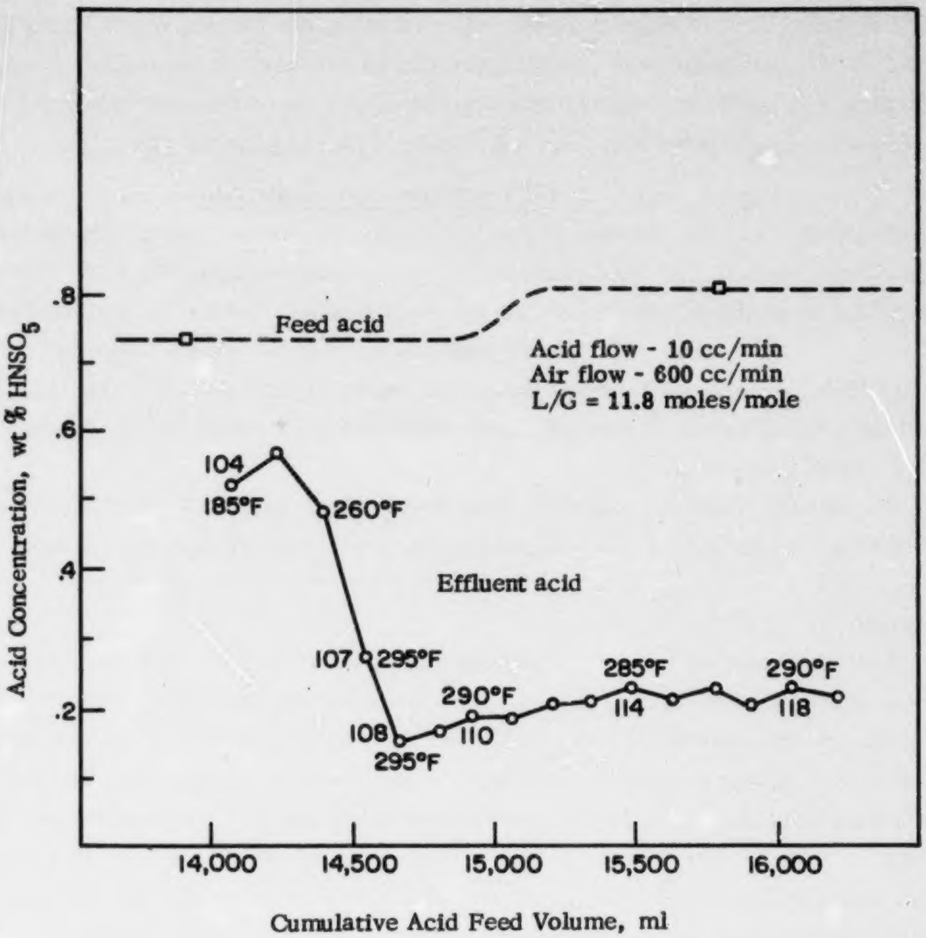


Fig. 13. Continuous stripper test: Experiment 1-D

Saenger, the vapor pressure of N_2O_3 above a 0.100 mole $HNSO_5/\ell$ solution in 80% H_2SO_4 would be 5.8mm Hg. So if the column were operating under equilibrium conditions with no catalytic activity, the partial pressure of nitrogen trioxide would be about half of the partial pressure that must exist in order for the experimentally determined degree of denitration to occur. The denitration is undoubtedly far more effective than this since it is highly likely that we are operating with such short contact times that we are nowhere near equilibrium. This was verified when additional experiments were run under the same conditions with inert packing (see below: experiments with column 2 with ceramic saddle packing).

Experiments 1-E, 1-F: multiple stage denitration — The effluent acid from experiment 1-D was saved and used as the feed stream for another denitration experiment run at 290 °F (experiment 1-E). This acid had a composite concentration of 0.320% $HNSO_5$. As shown in Fig. 14 at steady state at 290 °F, the column caused denitration to about 0.08% $HNSO_5$, again about 75% denitration. The effluent from this experiment, with a composite concentration of 0.110% $HNSO_5$, was passed through the column again (experiment 1-F, Fig. 15). The effluent from this third stage of stripping had a concentration of 0.03% $HNSO_5$, having had about 73% of its $HNSO_5$ removed.

The overall result of these three experiments (1-D, 1-E, 1-F) was that a nitrose of 0.800% $HNSO_5$ was denitrated to 0.030% $HNSO_5$ in three passes through the column. Thus, more than 96% of the $HNSO_5$ in the nitrose solution was removed by an effective bed depth of about 30 in.

Examination of the experimental conditions shows that the column was more effective than that. Each pass through the column removed about 75% of the $HNSO_5$, but the feed for each of the last two experiments was not the steady state effluent from the previous run. This was due to the fact that the feed streams were composites of the total run which included the higher strength effluent from the early parts of each run where the column was heating up. If the 0.800% $HNSO_5$ nitrose had been passed through 30 in. of carbon and each 10 in. accomplished the removal of 75% of the input nitrose (which seems to be a reasonable assumption in light of the experimental evidence), the final effluent would have been 0.013% $HNSO_5$. The overall effect is a denitration of more than 98%, closely approaching the desired 99% denitration level.

For the purpose of engineering design calculations, it is important to have some measure of the contact time between the acid, the air, and the charcoal catalyst. The residence time of the acid in the column is somewhat difficult to determine exactly because the difference in path length for the acid would create a distribution of residence times that would be dependent on the path configuration. This could be measured by use of a tracer material whose concentration in the acid effluent could be monitored, but this degree of sophistication is probably not necessary at this stage. A good preliminary design can be achieved by optimizing criteria which are easily available: L/G, acid space velocity, and gas space velocity.

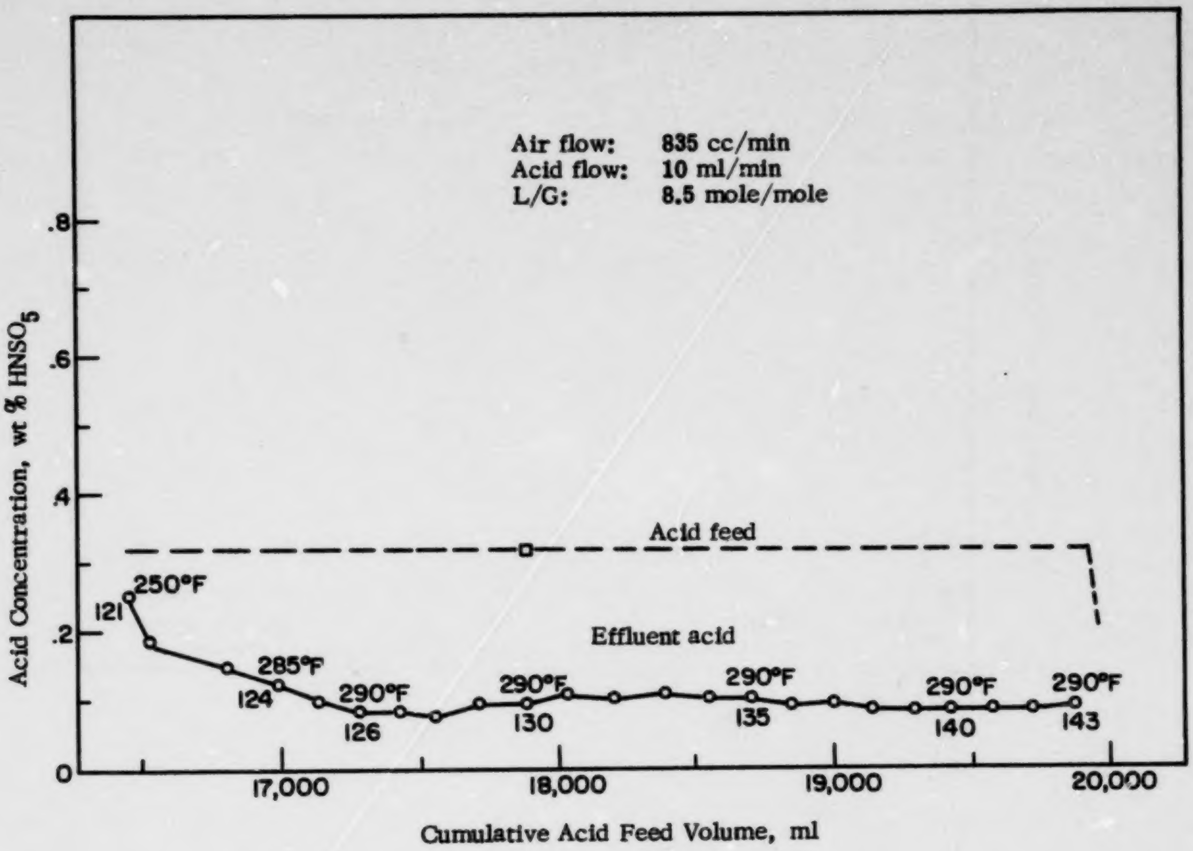


Fig. 14. Denitration of recycled acid: Experiment 1-E

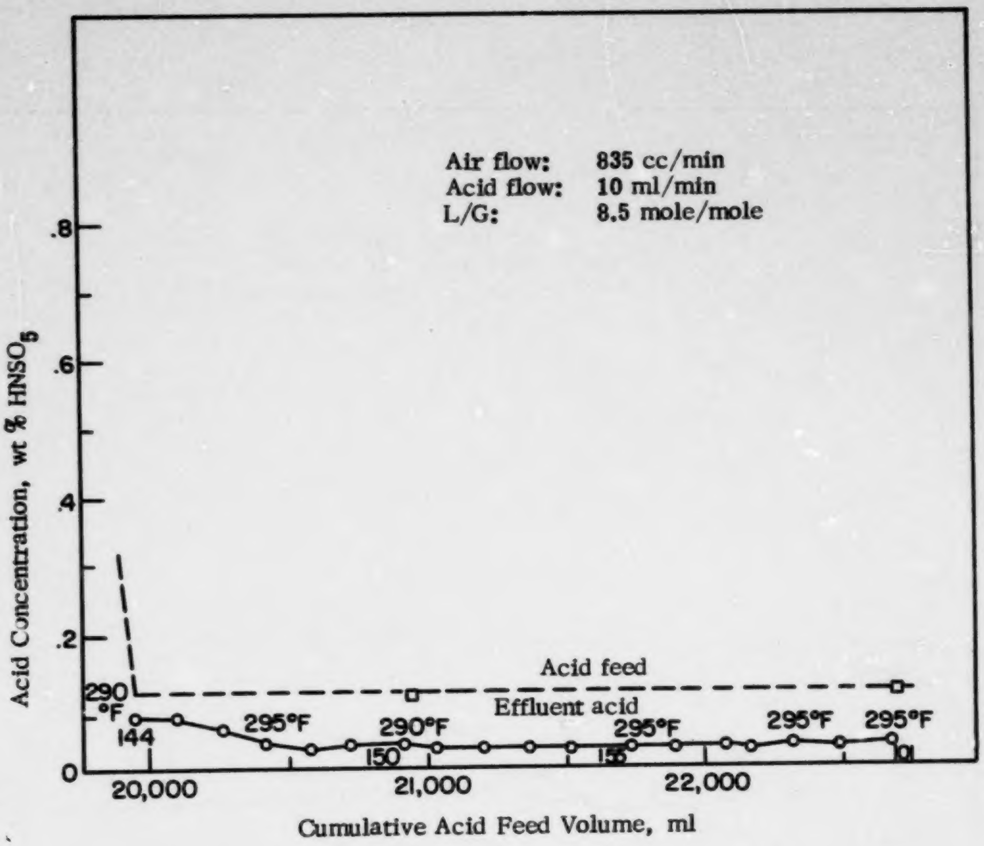


Fig. 15. Denitration of recycled acid: Experiment 1-F

The L/G for each run is indicated on the denitration graphs in this section of the report and varies between 3 and 30 moles of acid per mole of air, with values around 10 giving the best results. For an acid flow rate of 10 cc/min, the acid space velocity is 1.7 hr^{-1} (using the 350 cc void volume in the 2-in. × 10-in. charcoal bed and assuming 70% voids in the bed). On the same basis, a gas flow rate of 835 cc/min yields a gas space velocity of 140 hr^{-1} (STP).

Experiments 1-G, 1-H: air flow variation —— Experiments 1-A through 1-F were made without any effort to optimize the flow conditions of the column. Emphasis was on operating temperature and degree of denitration. A series of experiments was run where the degree of denitration was evaluated as a function of gas and liquid flow rates to try to develop preliminary estimates of flow parameters for future engineering design studies, as well as for the Tyco miniplant.

The first experiment, no. 1-G (Fig. 16), evaluated the effect of air flow rate on the degree of denitration. The column was started up and brought to steady state at about 260°F at point 167 using an air flow of 835 cc/min and an acid flow of 10 ml/min (L/G = 8.5 mole/mole). (Due to a change in the electrical hookup before this experiment, there was some difficulty in reaching 290°F. This was corrected after this experiment.) After data point 174 was taken, the air flow was decreased from 835 cc/min to 320 cc/min (L/G = 21.1 mole/mole). The temperature rose to about 270°F, and the degree of denitration was apparently reduced. After point 181, the air flow was further reduced to 96 cc/min (L/G = 74.3 mole/mole) giving a similar reaction in temperature and denitration.

Since the column was not operated at 290°F throughout experiment 1-G, it was decided to run the test over again at that temperature. Experiment 1-H shown in Fig. 17 was a repeat of the previous experiment except that the air flow variation was reversed: low flow at the start and high flow at the finish. The results of this experiment again show a general trend towards reduction in denitration as the air flow is reduced.

Experiment 1-I: acid flow rate variation —— The results of the previous experimentation indicated that for the 2-in. column being used it was necessary to pass 835 cc/min of air in order to effect 75% denitration of 10 cc/min of acid. Another experiment, no. 1-I, was run to see if it were possible to denitrate more acid with that same gas flow rate.

In this experiment, the L/G was doubled (to 17.0 mole/mole) by increasing the acid flow to 20 ml/min. As is shown in Fig. 18, the nitrosylsulfuric acid concentration of the nitrose was reduced from 0.79 to about 0.5%, a 37% reduction. It should be noted that, since the column activity had apparently dropped off somewhat during the last few experiments, this degree of denitration should be compared to the previous run no. 1-H which showed a 50% denitration level. In any case, it would seem that denitration is definitely a function of L/G under the conditions present in this series of experiments.

Experiment 1-J: cocurrent column operation —— In order to evaluate the catalytic stripper concept as completely as possible, the column was run under cocurrent gas/liquid contact conditions. The acid was fed to the top of the column at 10 ml/min, and the air was also fed to the top of the column at 835 cc/min. This experiment, no. 1-J, was performed at about 290°F and the results are shown in Fig. 19.

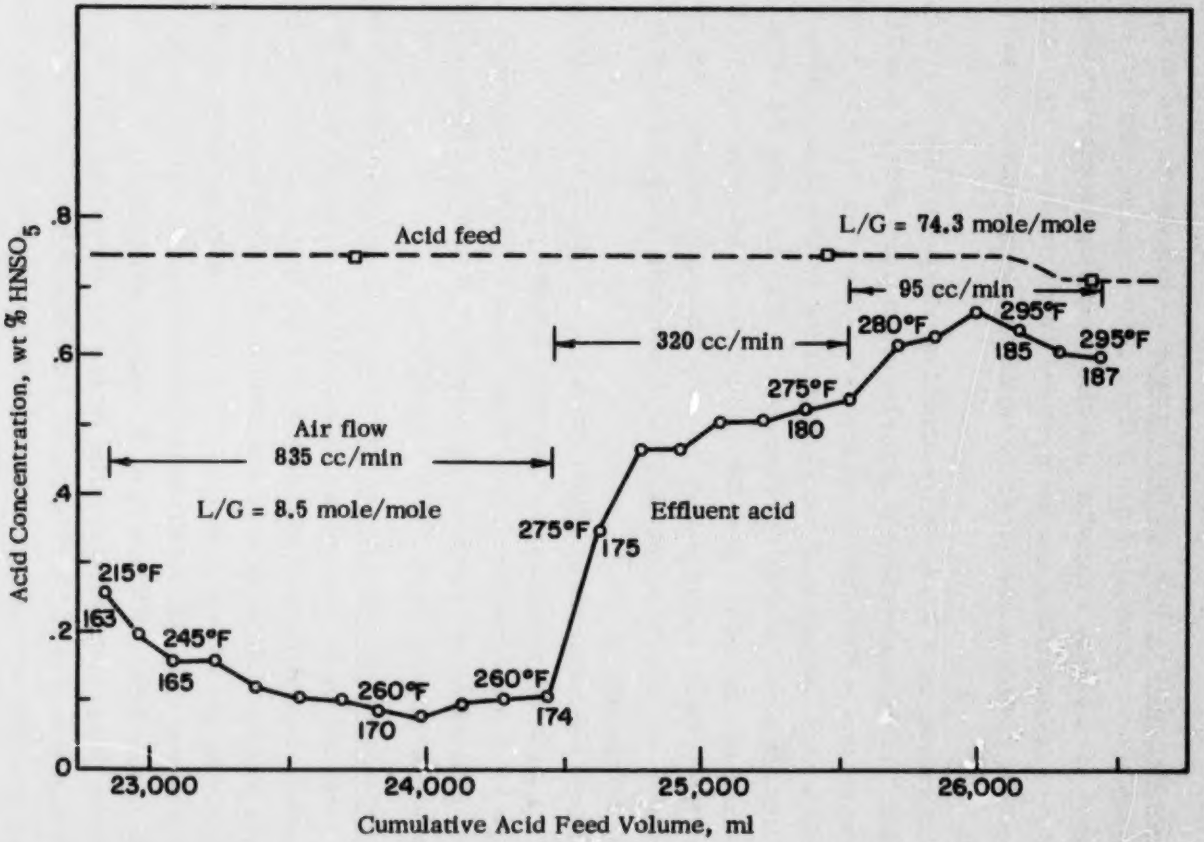


Fig. 16. Column optimization: Experiment 1-G, air flow rate variation

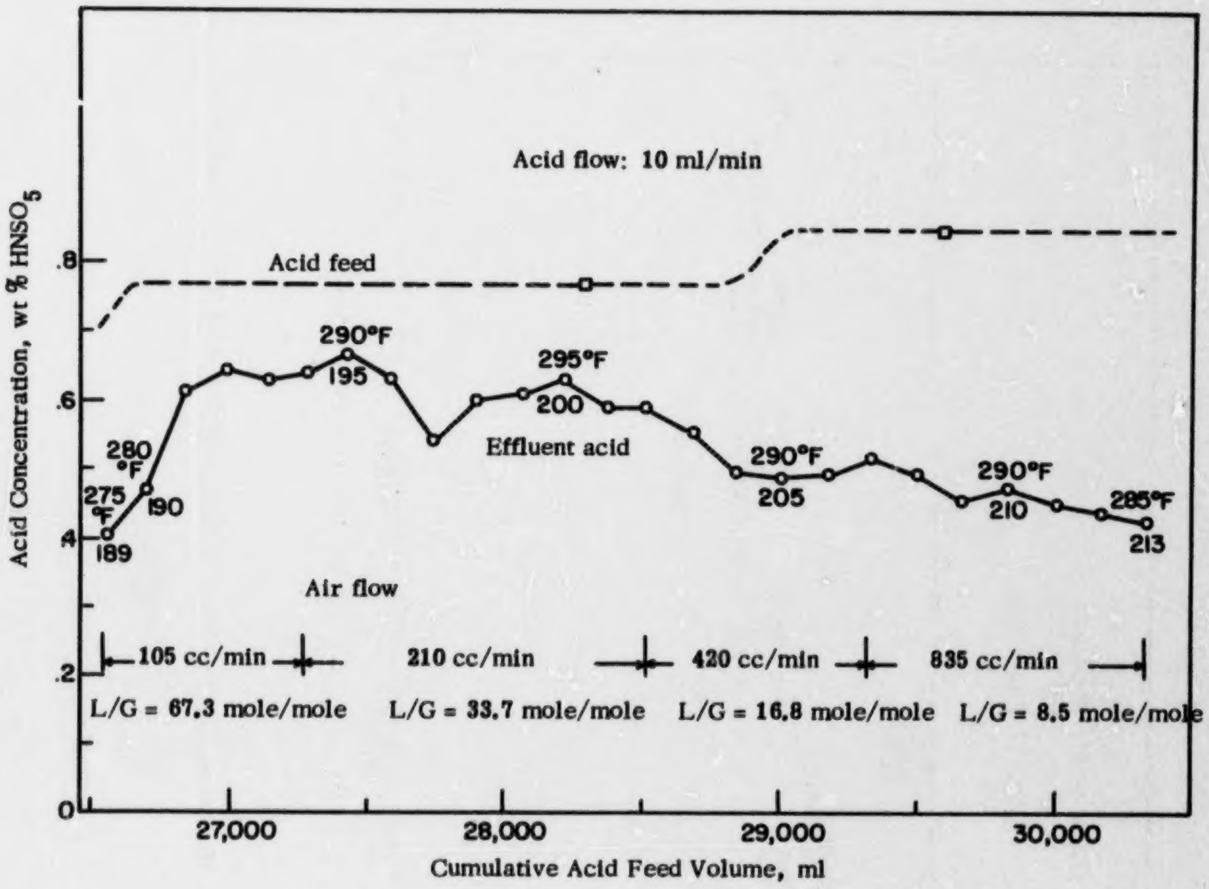


Fig. 17. Column optimization: Experiment 1-H, air flow rate variation

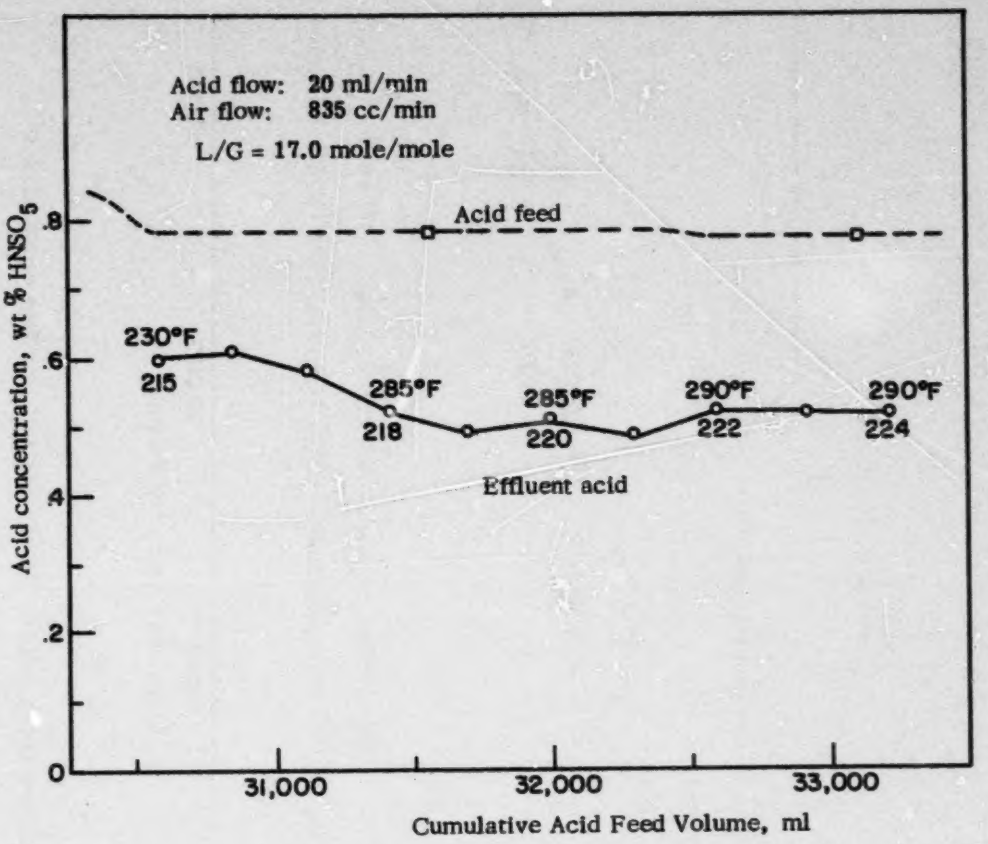


Fig. 18. Column optimization: Experiment 1-I, acid flow rate variation

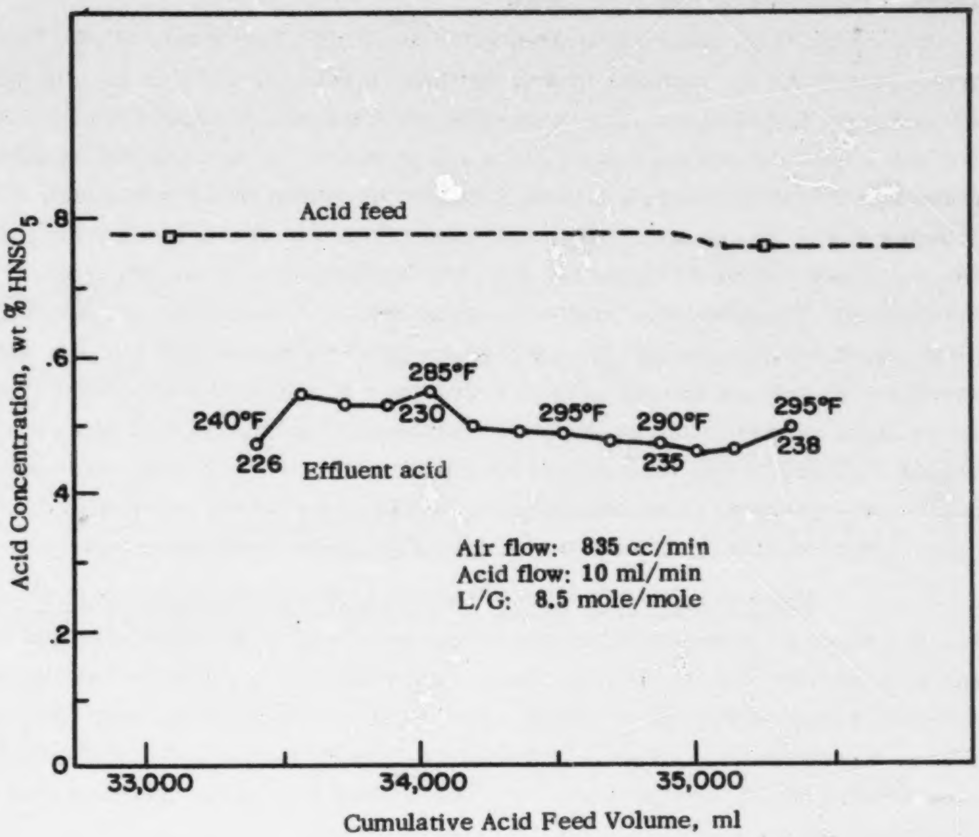


Fig. 19. Co-current flow: Experiment 1-J

Although the acid was denitrated only by about 40%, some interesting properties of this type of operation were noted. First of all the NO_2 in the exit gas stream appeared visually to be more concentrated than that in the countercurrent experiments. Infrared analysis of this exit gas clearly showed this level of NO_2 (about 5.4mm Hg partial pressure or about 0.7%) and permitted the calculation of a material balance within 13%, a precision that had not been easily obtainable in the countercurrent experiments.

At the same time, there was apparently far less water vapor in the exit gas stream which may account for the improved material balance. In the countercurrent experiments, there was a great deal of condensation at the point where the gas comes off the column because the exit line is not insulated and thus the gas is rapidly cooled. In the cocurrent experiment, the condensation must be taking place in the bottom of the column (which is relatively cool) and is removed with the exit acid. It appears, then, that the condensing water in the countercurrent experiments is scrubbing the exit gas, thus removing some of the NO_2 before it enters the infrared cell. To analyze this hypothesis, the countercurrent operation was carefully observed, and it could be seen that the water condensed all through the exit gas line, and at some times the exit gas actually bubbled through pools of condensed water. Some of this condensed liquid was removed from the system and analyzed and was found to be very acidic (about pH 0.5). Thus, the NO_2 was reacting with the water to form nitric acid. These points do not make a case for the cocurrent operation of the stripper but the experimentation does provide some insight into the operation of the countercurrent operation of the column.

Experiments 1-K, 1-L: evaluation of apparent catalyst deactivation — Experiments 1-H and 1-I showed an apparent reduction in activity of the activated carbon in column 1. At the time when no. 1-H was started, more then 26 ℓ of nitrose solution at high temperature had passed through the column, but from all external evidence very little change could be seen in the carbon. There had been some carbon fines removed during the first experiment, but the effluent acid had been free of particulates ever since. Had the carbon really lost its activity and if so, why?

Experiment 1-K was run to see if the catalyst had lost its activity. Experimental conditions were virtually identical with those of run no. 1-D which showed about 75% denitration. The results (see Fig. 20) showed that the 0.760% $HNSO_5$ feed solution was denitrated to 0.320% for a denitration of 58%. This is a significantly lower level of catalyst activity similar to the results of experiment 1-H.

In evaluating this apparent deactivation, two mechanisms were considered: (1) physical deterioration, and (2) chemical poisoning. As was mentioned above, there was no evidence of physical breakdown of the carbon as might be measured by the production of fines during operation, and in addition, a visual examination of the carbon through the glass walls of the column showed no gross change in the size or shape of the particles. The conclusion was made that the deactivation was chemical in nature.

Since the only materials that entered the column were air and nitrosylsulfuric acid solution, it was concluded that the poison must be entering with the acid. Physical examination

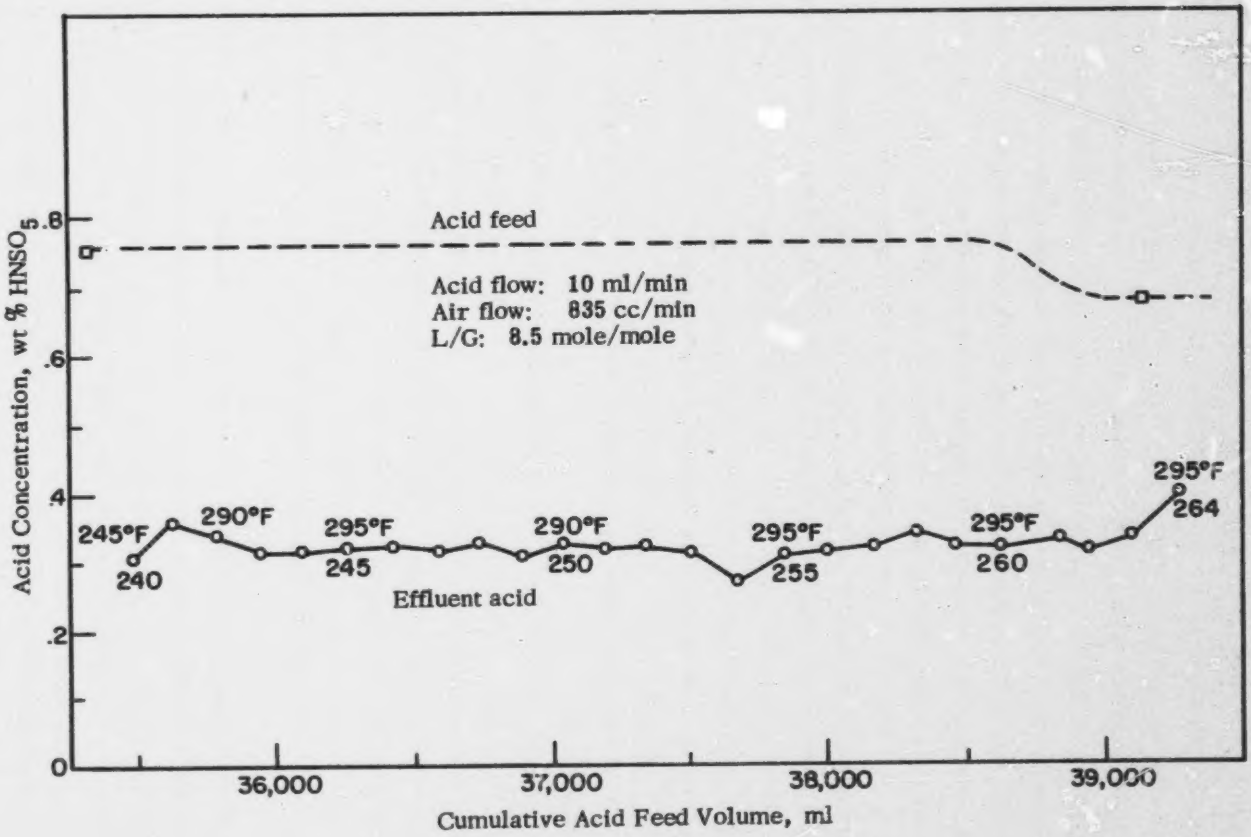


Fig. 20. Countercurrent column operation: Experiment 1-K

of the acid plus observations of earlier experiments gave a clue to the possible source of the poison. The acid that had been used throughout the stripper evaluation was 80% H_2SO_4 that had been purchased in bulk about a year prior to use. About 2000 lb of this commercial grade acid had been purchased from a local supplier in order to avoid the problem in diluting large quantities of acid. The acid had been stored in special acid resistant black polyethylene carboys. When fresh, the acid had been almost water white in color, but more recently it had been noticed that it was now brownish in color although still clear. A check with the supplier, Nyanza Chemical, revealed that the color was due to some carbonization of the polyethylene as well as some leaching of carbon filler from the black polyethylene carboy. Titration of the fresh acid with $KMnO_4$ showed the requirement for a negligible amount of the oxidizing agent to form the characteristic purple end point. It was therefore initially assumed that the discolored acid was not interfering with the analysis of the nitrose solution.

However, it was observed in early experiments that the effluent acid from the stripper was noticeably lighter in color than the feed acid. Thus, the charcoal was decolorizing the acid. Since the deactivation was observed, a comparison was made among several column effluent solutions that had been saved from runs made over a period of time, and it was noted that the early effluents were obviously decolorized but the latest runs were not. The ability of the carbon to adsorb the color-producing material from the acid had definitely been sharply reduced. If the carbon's adsorption sites for decolorizing were the same as the catalytic sites for nitrose oxidation, it would be possible to explain the reason for the stripper deactivation.

In order to properly analyze the solutions for evidence to support this hypothesis, it was necessary to develop another technique for measuring the nitrogen oxide content of the acid solutions. The method chosen was the nitrometer, an apparatus widely mentioned in the literature as appropriate for this purpose. The technique involves the reaction of fixed nitrogen in solution with mercury resulting in the evolution of nitric oxide. The volume of the NO is measured, thus permitting the calculation of the NO_x content of the original solution. The procedure is somewhat more time consuming than the $KMnO_4$ titration which is why it was not used originally.

A series of experiments was performed to determine if the 40 ℓ of contaminated commercial acid had deposited sufficient material on the carbon to reduce its catalytic activity. First, the column was used to denitrate a nitrose solution under conditions almost identical to run no. 1-D, except that reagent grade acid was used to make up the nitrose. This test, experiment 1-L, again appeared to demonstrate that the catalyst activity had been reduced with the carbon achieving only about 40% denitration of the nitrose (see Fig. 21). What was more significant was that the effluent acid was strongly discolored although the feed acid was water white. It appeared that the more pure nitrose was causing the desorption of the contaminant that had been loading the catalyst.

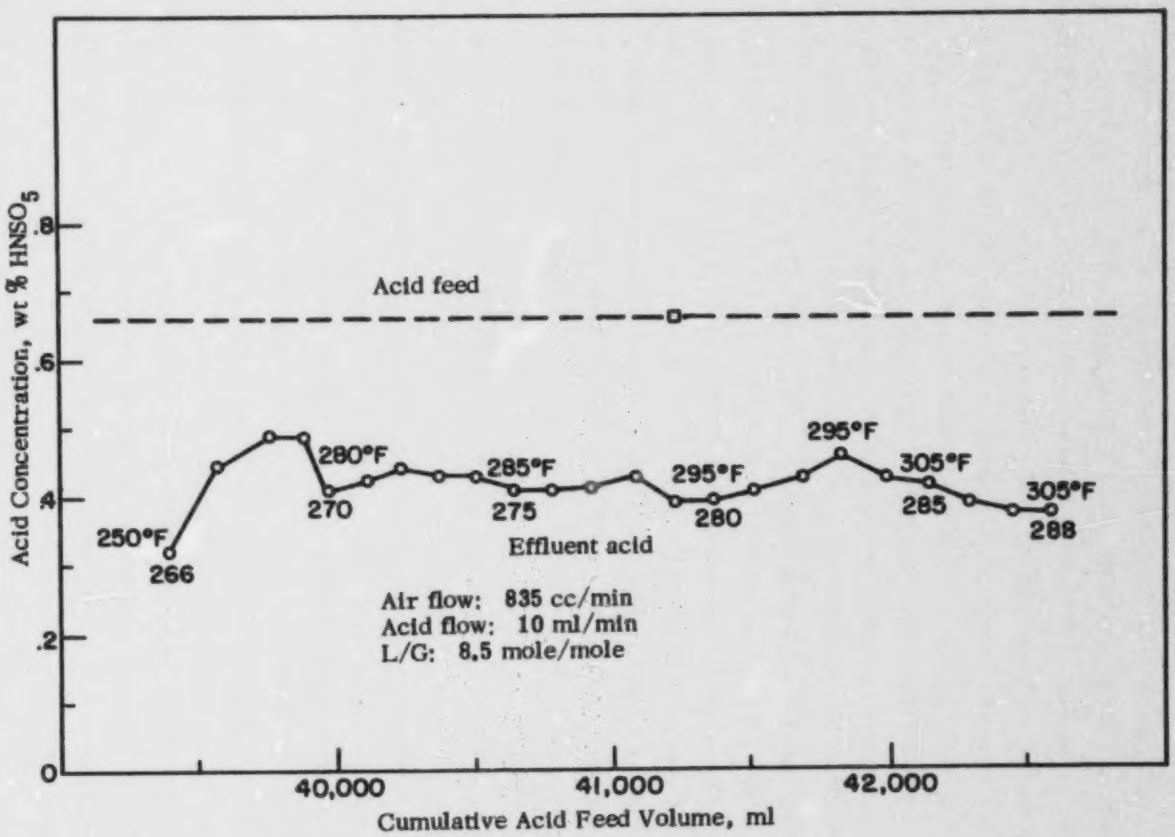


Fig. 21. Denitration using reagent grade acid in nitrose: Experiment 1-L

To continue this cleaning, it was decided to wash the column with hot reagent grade acid rather than nitrose made from this acid. The first liter of acid (which passed through the column at about 175 °F) was made up of 96% reagent grade acid and resulted in a very dark effluent. The second liter of wash solution was 80% reagent grade acid and came out of the column almost as clean as it went in. It was hard to tell if the concentrated acid had attacked the carbon or if it had just accelerated the cleaning of the column. To test this, a small amount of fresh carbon was heated to 175 °F in 96% reagent grade acid. The acid turned inky black apparently with carbon fines. The acid was drained off and the test repeated with more acid. No more fines were visible although the acid turned greenish in color completely different from the effluent from the column. It was therefore assumed that the 96% acid had accelerated the washing of the column and was not causing the breakdown of the carbon. As further support for this conclusion, the effluent from the column was centrifuged for 30 min without obtaining any sediment. Previous attempts to centrifuge effluent solutions which appeared to show carbon fines (as when fresh carbon was treated with nitrose) had resulted in partial clarification and the collection of sediment.

In order to put all these data in perspective and obtain a quantitative approach to the problem, several solutions were analyzed both by titration and with the nitrometer. The results of these analyses are shown in Table V. The first test on the fresh acid indicates that there is some oxidizable material in the acid that contains no fixed nitrogen. It is present in very low concentrations which justifies the original assumption that it would not interfere with individual acid analyses. Test 2 shows no reactive species detectable in the reagent grade acid by either test.

The third set of analyses shows a reproducible difference in $HNSO_5$ concentration when performed by $KMnO_4$ titration as compared to nitrometer testing. The fact that the titration is consistently low is attributed to a small loss in NO_x during titration because the sample heats up due to the exothermic oxidation, thus vaporizing some dissolved nitrogen oxides. The difference between the two techniques appears to be fairly constant at about 5%.

The fourth test shows that the $HNSO_5$ analysis when using barrel acid exhibits a smaller difference between the $KMnO_4$ titration and the nitrometer than when using reagent grade acid, possibly because of the contamination in the barrel acid.

The fifth test shows about 10% more "$HNSO_5$" by titration than by nitrometer. Since the titration had been running lower than the nitrometer on standardization sample as discussed above, this 10% increase is quite significant. It appears to be due to the removal of some oxidizable material from the column.

Test 6 performed on the effluent from the attempt to denitrate reagent grade acid shows a 20% higher $HNSO_5$ concentration by titration than by nitrometer. Here the clean acid appears to be rapidly washing out the contaminant from the carbon.

The results of test 7 clearly show that there are oxidizable species in the column that contain no oxides of nitrogen. This result in conjunction with the others above appears to give

Table V. Comparative Analyses of Acid Samples

	Sample	$HNSO_5$ Concentration, %*	
		$KMnO_4$ Titration	Nitrometer
1.	Fresh barrel acid†	0.0037	nil
2.	Reagent grade acid (80%)	nil	nil
3.	Reagent grade acid plus $HNSO_5$	0.628 0.630	0.664 0.670
4.	Barrel acid plus $HNSO_5$	0.655	0.667
5.	Effluent from stripper run no. 1-G	0.368	0.333
6.	Effluent from stripper run no. 1-L	0.480 0.485	0.385 0.415
7.	Effluent from reagent grade acid wash‡	0.197	0.030

---

[*] All results are reported as apparent $HNSO_5$ concentrations even where the $KMnO_4$ titration is clearly measuring species other than NO_x.

[†] Barrel acid refers to 80% H_2SO_4 that had been stored in black plastic carboys for about 1 yr.

[‡] This is a mixture of 96% and 80% acids from the 175 °F columns wash described in the text.

strong support to the original hypothesis that the column adsorbed some contaminant, probably organic, which partially poisoned the column of activated carbon. In actual use, this type of poisoning should not be a factor since flue gas does not contain similar contaminants.

4. Testing with column 2 - experiment 2

In order to determine the effect of vapor pressure denitration (thermal stripping) on the operation of the stripper column, an experiment was run using ceramic saddles in the column instead of activated charcoal. Column no. 2 was set up so that it was physically the same as column 1 (except for the difference in surface area between the ceramic saddles and activated charcoal): three beds in series containing about 30 cu in. of saddles to a depth of about 10 in. Experiment 2 was run at about 290 °F with flow rates of 10 ml/min of acid and 835 cc/min of air. These conditions were identical with those in experiment 1-D which showed about 75% denitration.

Fig. 22 shows the results of experiment 2 with the 0.670% $HNSO_5$ feed acid being denitrated to about 0.570% $HNSO_5$. This is a denitration level of 15%, obviously far lower than that achieved with the activated charcoal.

At equilibrium at 290 °F with the acid and gas flow rates and concentrations as present in this experiment, the acid should have been denitrated to about 0.31% $HNSO_5$. Clearly, the column conditions were far from equilibrium.

A somewhat unusual aspect of the experiment was the fact that at the beginning of the experiment the effluent acid had a considerably higher $HNSO_5$ concentration than the feed acid. Since this is impossible, it is necessary to examine the conditions and the analytical technique to explain the situation.

The analysis for $HNSO_5$ in sulfuric acid is accomplished by titrating the acid with potassium permanganate, a strong oxidizing reagent. The $KMnO_4$ oxidizes the NO_x content of the acid to HNO_3 and thus allows the calculation of the amount of fixed nitrogen in the acid solution. However, the $KMnO_4$ titration is not specific for NO_x but will react with any oxidizable material in solution. What must have occurred in this experiment is that there was some contaminant on the fresh saddles, perhaps an organic of some sort, and the sulfuric acid washed the material off the saddles. When the effluent was titrated, the $KMnO_4$ reacted with both the NO_x in solution and the organic contaminant, thus showing a high apparent $HNSO_5$ concentration. This contaminant was eventually washed off the saddles and the steady state effluent concentration shown after point 6 was apparently due only to $HNSO_5$.

5. Testing with column 3

A total of five runs were made on column 3 which consisted of one 22-in. bed of activated charcoal in a 2-in. column. Nitrose and air were passed in countercurrent streams and the gas and acid streams analyzed as in previous tests. All five test runs were made at steady state temperatures of 290 °F with fluid flows being held constant at 10 ml/min for the acid and 835 cc/min for the air. The nitrose concentration was in the 0.5 to 0.6% $HNSO_5$ range.

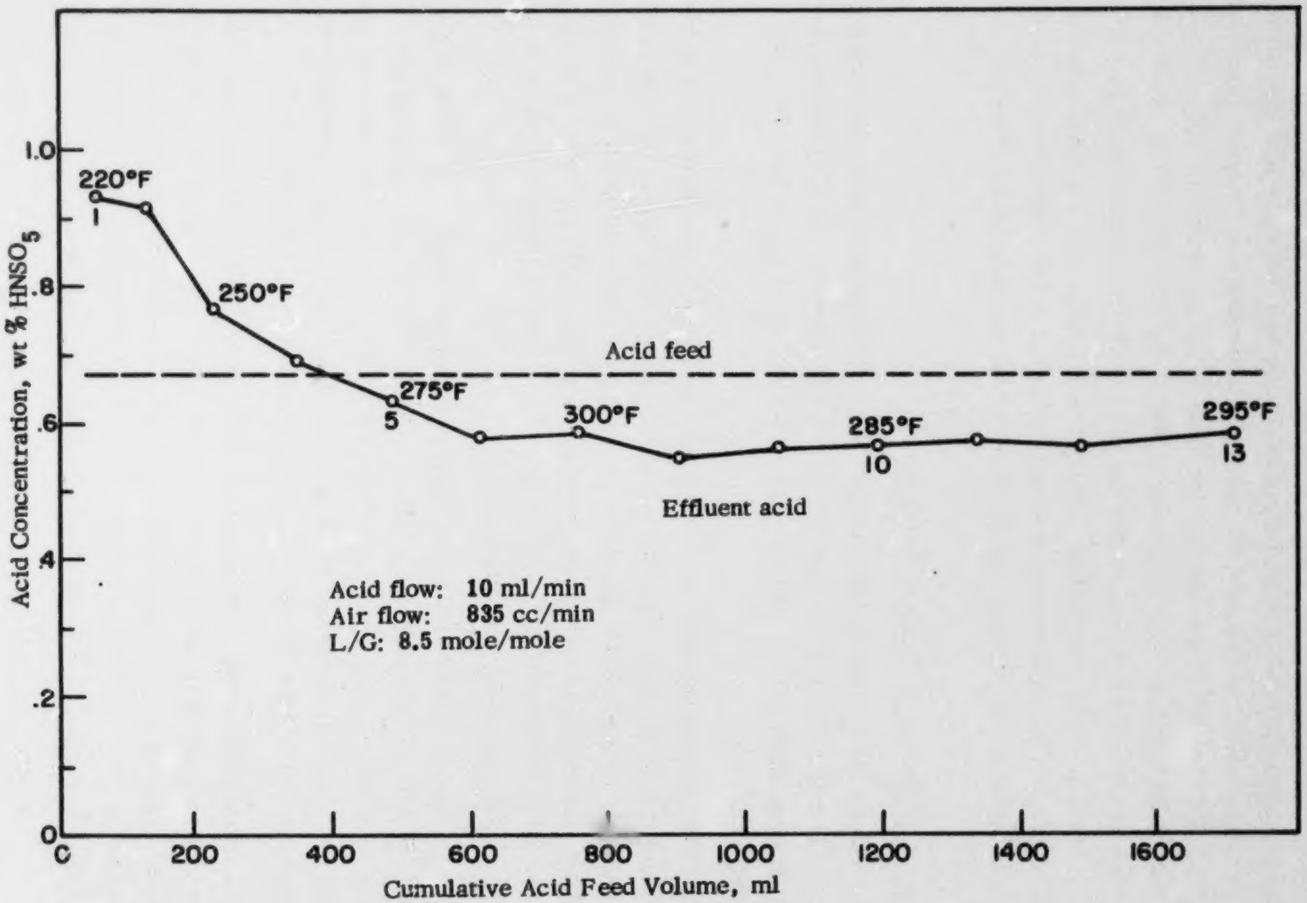


Fig. 22. Stripper blank - saddle packing: Experiment 2-A

A total of 14 ℓ of nitrose were passed through the column during five runs (totaling about 25 hr of operation) and after an initial period where impurities were washed out of the carbon, the effluent acid maintained a concentration of less than 0.007% $HNSO_5$, which represented a denitration of about 99%. Analysis of these extremely low concentrations was quite difficult, and a technique was used that gave the maximum possible $HNSO_5$ content rather than an exact figure. Instead of titrating the acid solution to an end point (which was very difficult to see at these low concentrations), a given amount of $KMnO_4$ was introduced into an aliquot of the acid. If this amount of reagent showed that the end point had been exceeded (which it invariably did), it could be safely said that the $HNSO_5$ concentration was less than an amount equivalent to the $KMnO_4$ added. The amount used was equivalent to 99% denitration, so it is a fair statement that, under the steady state conditions indicated above, denitration was greater than 99% complete.

D. Summary of Results of Charcoal Evaluation

The tests with the Witco activated charcoal in batch and continuous equipment has produced positive results which verify the concept of the catalytic stripper and indicate that the charcoal can be used for denitration of nitrosylsulfuric acid solutions in the Tyco Catalytic Chamber Process:

1. The apparent physical instability of the carbon particles observed in earlier testing has been shown to be temporary in nature. Initial contact of the carbon with hot nitrose results in the production of fines which apparently result from initial rapid reaction on the charcoal surface. After a short period of time, the production of fines stops and there is no further physical breakdown of the particles. At the same time, there is no apparent reduction in catalytic activity when the carbon is stabilized.

2. The reaction of the carbon with oxides of nitrogen which resulted in the production of nitrous oxide (N_2O) is apparently a minor problem. The amount of N_2O produced is a negligible fraction of the total NO_x content of the stripper effluent gas and should have no effect on either the long term stability of the carbon or the efficiency of NO_x recovery in the process. (N_2O concentrations in stripper off-gas samples were consistently less than 10 ppm.)

3. Denitration of nitrose solutions in the 1% $HNSO_5$ concentration range is in excess of 99% in columns containing 22 in. of activated charcoal, with acid space velocities on the order of 0.8 hr^{-1}, gas space velocities of 65 hr^{-1}, and L/G values of 8.5 mole/mole. These figures are based on the experimental conditions used in the testing and do not indicate optimum values, although they do suggest starting points for engineering scaleup.

IV. HIGH TEMPERATURE SCRUBBER - LABORATORY EVALUATION

A. Background

Small scale laboratory experiments during the previous contract showed that oxides of nitrogen could be absorbed in sulfuric acid from a nitrogen carrier gas stream at 250°F with high recovery efficiencies. Replicated runs in a 1 1/2-in.-diameter column packed with Berl saddles to a depth of 24 in. demonstrated greater than 98% scrubbing efficiency at 255°F at an L/G of about 1.7 mole/mole. Preliminary evaluation of the high temperature scrubbing concept in the 10 SCFM miniplant verified this absorption capability. Because of the need for scaleup data which were not available from previous test runs, it was decided to construct a more sophisticated laboratory scrubber and investigate the characteristics of the high temperature scrubber on a broader basis.

B. Equipment Design

A laboratory scale scrubber was designed based on the Corning flanged pipe system to permit modular construction. Fig. 23 shows a schematic diagram of the scrubber which is made of 2-in. Corning flanged pipe with feed lines consisting of 1-in. pipe and transfer lines made of 1/4-in. pipe. A photo of the apparatus is shown in Fig. 24.

Acid was pumped through a 1-in.-diameter section which was wrapped with heating tapes capable of heating the acid to temperatures in excess of 250°F. The acid was pumped with a peristaltic pump capable of delivering flows up to about 300 ml/min. The acid outlet had a reservoir section to act as a gas trap with acid samples being taken periodically to drain the system and to permit analysis of the acid. The column was heated with external heating tapes and was packed with 40 in. of 1/4-in. Intalox saddles. There was one redistributer half-way up the column, and observation of fluid flow in the column showed good distribution of flow across the column.

C. Operating Conditions

The column was operated by contacting a NO_x-bearing gas with sulfuric acid in a countercurrent mode. The gas was prepared by mixing a nitrogen carrier gas with N_2O_3, the latter being supplied as the trioxide in commercially available gas cylinders. The acid was the same material used in the continuous column tests for activated charcoal analysis: 80% sulfuric acid, commercial grade.

The flow rates used in the column were calculated based on standard theoretical assumptions. Given the L/G, the type and size of the packing, and the column diameter, it was possible to calculate the flooding velocity of the column. Making the assumption that the optimum gas velocity is one-half the flooding velocity, the optimum gas and liquid flow rates could be

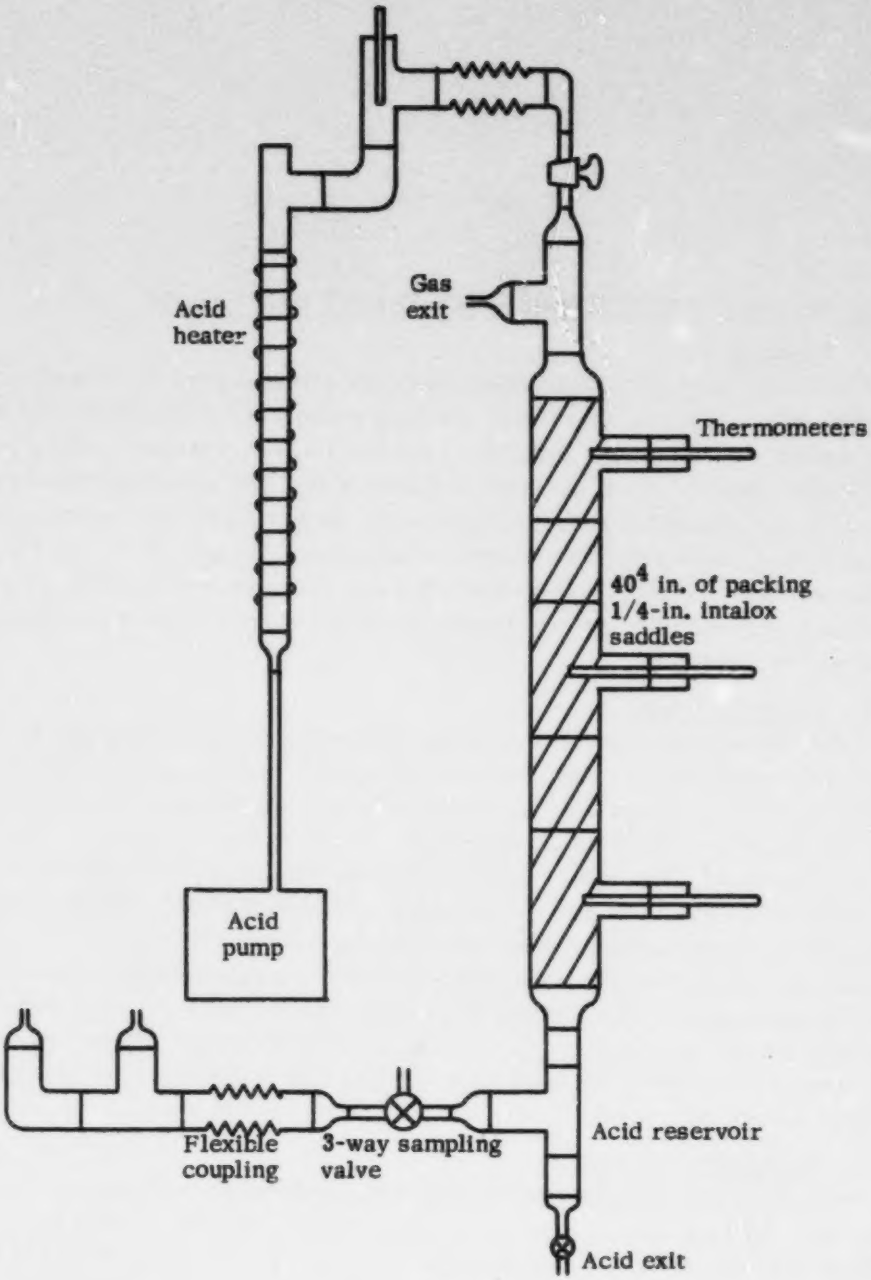

Gas exit
Acid heater
Thermometers
40⁴ in. of packing 1/4-in. intalox saddles
Acid pump
Flexible coupling
3-way sampling valve
Acid reservoir
Acid exit

Fig. 23. Laboratory scale high temperature absorption column

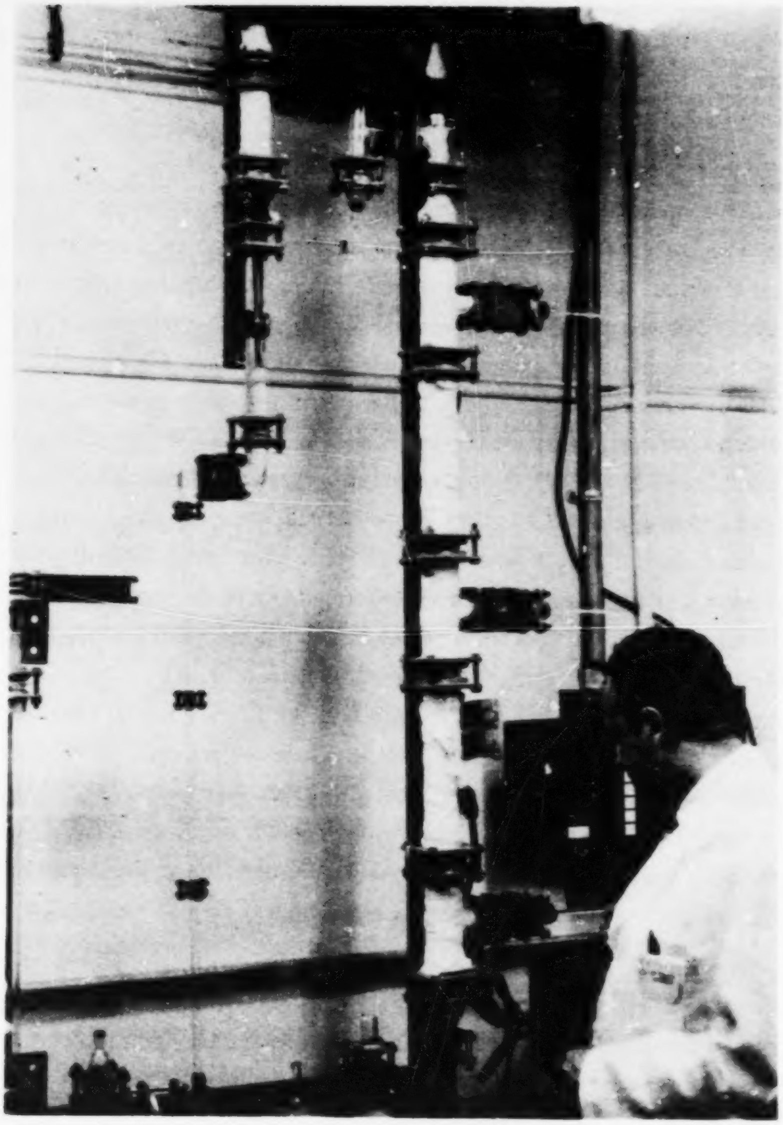


Fig. 24. Laboratory apparatus for continuous evaluation of high temperature scrubber

obtained. These flow rates were:

Nitrogen carrier gas	66,201 cc/min (2.35 SCFM) at STP
N_2O_3	232 cc/min (3500 ppm by volume) at STP
Sulfuric acid (80% H_2SO_4)	205 cc/min (at 70 °F)

These figures are based on L/G of 2.1 mole/mole with a column operating temperature of 250 °F. It was intended that the L/G be varied as well as the basic gas flow rates. As will be seen in the discussion of the results, the carrier gas flow was varied between 11,500 and 54,000 cc/min and the L/G between 2.0 and 10.0 mole/mole.

D. Analytical Techniques

The inlet gas was analyzed by taking a sidestream from the gas feed and running it through the infrared analysis cell. This is a batch technique and requires about 30 min to run, 10 min to pass the sample through the cell, 13 min to run the infrared spectrum and 5 to 10 min handling time. The analysis is based on calibration curves obtained previously and is considered to be quite accurate and reproducible. Error is less than 5%.

The outlet gas was analyzed by first freezing out the water vapor and then running the gas through the infrared cell. The water was trapped by passing it through a saddle-filled U-tube immersed in alcohol at -45 °C. Considering that trapping of the water might well remove NO_2 from the gas stream, provisions were made for analyzing the NO_x content of the trapped solution. After each experiment, a quantity of 3% H_2O_2 was added to the trap which was then sealed off to prevent gas leakage. The trap was warmed up to thaw out the frozen trapped water and the U-tube shaken for several minutes to absorb the gaseous NO_x. The liquid was decanted and the trap rinsed twice to collect the total dissolved NO_x. The peroxide solution plus the washings were titrated with standard NaOH to measure the NO_x content. The results invariably showed a negligible amount of NO_x absorbed in the water.

The outlet acid was analyzed by titration with $KMnO_4$ as previously discussed in connection with the stripper experiments. The nitrometer was not used.

The inlet acid was fresh material taken from the barrel and was considered free of NO_x (see Table V for analysis of the NO_x content in fresh barrel acid). The acid was not recycled.

E. Experimental Results

A total of 20 test runs were made with the apparatus with the experimental conditions and test results given in Tables VI and VII. The first significant point to be noted in the data is the wide variation in the NO_2/NO ratio in the inlet gas, despite the fact that gases obtained from both Matheson and Air Products were claimed to have a mole ratio of 1:1. This erratic gas concentration variation seemed independent of the technique used to withdraw the gas from the cylinder. Nitrogen trioxide is made available as a liquid under pressure, and it is possible to withdraw the material as either a gas or a liquid from the cylinder. In the first three runs (Table VI), the N_2O_3 was removed as a liquid and completely volatized in the line, while in the remaining tests the gas above the liquid was withdrawn.

Despite the problems in providing the proper gas mixture, there is much to be gained from these experiments. The most obvious point is that the gas side efficiency is consistently

Table VI. High Temperature Scrubber Experimental Results 250°F Steady State Operation
2-in. × 40-in. Column Packed With 1/4-in. Porcelain Intalox Saddles

Experiment No.		1	2	3	4	5	6	7	8	9	10
Inlet NO_2, ppm		5000	4600	2000	4000	1500	3700	4200	1600	1000	1200
Concentration, mm Hg*	NO	2900	2900	1000	3600	2400	3300	2800	2100	2000	2700
NO_x content, % by volume		7900	7500	3000	7800	3900	7000	7000	3700	3000	3900
Total gas flow, ℓ/min (STP)		11.5	11.5	11.5	11.5	11.5	15.0	23.0	17.0	34.5	27.5
Acid flow, cc/min (70 °F)†		52	58	50	100	150	66	100	50	100	100
L/G mole/mole		3.6	4.0	3.5	6.9	10.4	3.5	3.5	2.4	2.3	2.9
Material balance error, % ‡		20	15.8	13.3	§	2.8	73.5	26.5	29.5	11.6	10.6
Gas side absorption efficiency, % **		77.6	96.9	72.7	82.8	93.1	97.5	98.5	98.4	95.8	95.7
Acid side adsorption efficiency, % ***		57	81.1	61.3	§	65.0	24.0	72.0	67.0	84.2	84.0

Notes:

* As measured by infrared analysis.

† As measured by outlet acid flow at about 200 °F.

‡ % Material balance error $= \dfrac{\text{Inlet } NO_x \text{ (gas)} - \text{Outlet } NO_x \text{ (acid + gas)}}{\text{Inlet } NO_x \text{ (gas)}} = \times 100.$

§ Material balance error negative, greater than 100% acid side absorption efficiency.

** Efficiency based on effluent gas and feed gas.

*** Efficiency based on effluent acid and feed gas.

Table VII. High Temperature Scrubber Experimental Results 250° F Steady State Operation 2-in. × 40-in. Column Packed With 1/4-in. Porcelain Intelox Saddles

Experiment No.	11	12	13	14	16	17	19	20
Inlet NO_2, ppm	13,200	2500	4200	5500	3300	1700	2000	2100
Inlet NO, ppm	5000	5600	3200	3000	4300	6600	6100	4100
Total Inlet NO_x, ppm	18,200	8100	7400	8500	7600	8300	8100	6200
Total gas flow, ℓ/min (STP)	54.5	35.0	52.0	52.0	20.0	29.5	20.0	20.0
Acid flow, cc/min (70 °F) ‡	150	100	150	150	100	150	100	100
L/G mole/mole	2.2	2.3	2.3	2.3	4.0	4.0	4.0	4.0
Material balance error, % §	4.8	8.7	8.8	7.1	1.6	3.1	10.4	−6.1
Gas side absorption efficiency, %*	84.8	78.5	97.7	95.4	88.1	96.4	80.0	83.7
Acid side absorption efficiency, %**	80.0	69.8	88.9	88.8	86.3	90.4	69.6	89.8

Notes:

† As measured by infrared analysis.

‡ As measured by outlet acid flow at about 200 °F.

§ % Material balance error = $\dfrac{\text{Inlet } NO_x \text{ (gas)} - \text{Outlet } NO_x \text{ (acid + gas)}}{\text{Inlet } NO_x \text{ (gas)}} \times 100.$

* Efficiency based on effluent gas and feed gas (infrared analysis).

** Efficiency based on effluent acid and feed gas.

high, indicating that the scrubber is doing an excellent job in removing the oxides of nitrogen from the gas stream. Since both the inlet and outlet gas analyses are based on the same calibration curves and are thus independent, these high removal efficiencies can be considered quite reliable. (It should be noted that these results closely reproduce the original experiments described in the final report for Contract PH-86-68-75.)

The problem is, of course, that the acid side efficiencies do not agree with the gas based figures and thus the material balances do not close. There are some general trends which might help to explain the discrepancies. First of all one might expect these large material balance errors because of the variations in the inlet gas NO/NO_2 ratio. Some of these runs were made successively on the same day, yet there was still considerable variation in the inlet gas composition. It is therefore reasonable to assume that there might have been some change in the inlet gas composition from the time the inlet gas was analyzed to when the outlet gas was analyzed.

If the NO_2 is reacting with the water in the 80% H_2SO_4 to form HNO_3 in the outlet acid, it would not have been detected by titration with $KMnO_4$ which only determines oxidizable species. Nitric acid can only be determined by measuring total nitrogen oxides with the nitrometer and subtracting the oxidizable nitrogen oxides obtained by $KMnO_4$ titration. The difference must be fully oxidized NO_3^-. This type of analysis was performed on a portion of a large composite sample obtained from several of the first eight runs. It was found that the nitrometer analysis of NO_x was about 8% higher than the $KMnO_4$ titration value, which is a major portion of the material balance error in most of the first eight runs. It is interesting to note that in the remainder of the runs there was usually an excess of NO and the material balances closed better. NO of course does not dissolve in or react with sulfuric acid and it might be expected that the material balance would be better in these cases.

The fact that there was an excess of NO in many of the runs leads to an interesting analysis of the data. It is significant to note that, despite the imbalance in the NO_2/NO ratio, the absorption efficiency in the scrubber remained consistently high. If the absorption was assumed to take place through the mechanism of equimolar combination of NO and NO_2 with H_2SO_4, then a maximum absorption efficiency could be calculated for each run. For example, in run no. 17, the entering gas contained 1.3 mm Hg of NO_2 and 5.0 mm Hg of NO so the maximum absorption should have been 1.3 mm Hg of NO_2 and 1.3 mm Hg of NO, or 2.6 mm Hg NO_x out of a total of 6.3 mm Hg of NO_x for an overall efficiency of 36%. In this case, the measured overall scrubbing efficiency was 96.4%, far more than is theoretically possible.

This phenomenon is hard to explain until one examines the outlet gas concentration for several of the experimental runs and observes that there is a considerable amount of NO_2 present even though it was NO that was present in excess in the inlet gas. If one considers that there is a considerable delay (approximately 10 min) between gas sampling and the time when the infrared spectrum is obtained, it seems quite likely that some oxygen has been introduced into the gas between the delivery of the NO_x from the N_2O_3 tank and the time when the gas is fed to the infrared cell.

If oxygen were present in the gas as it was fed to the scrubber, some of the NO would have been oxidized to NO_2 thus forming a more equimolar mixture of the two nitrogen oxides and allowing the absorption of more NO_x than would have been possible based on the original feed gas analysis. If relatively high absorptions were assumed in the scrubber based on the combination of equimolar amounts of NO and NO_2, then there should be low concentrations of NO_2 in the outlet gas. The fact that there was consistently large amounts of NO_2 compared to the NO in the outlet gas suggests that the NO continued to oxidize due to the presence of oxygen and by the time the gas was analyzed much of the NO had been oxidized.

To check this hypothesis, several runs were made with a feed gas consisting of nitrogen and NO with no NO_2 be intentionally fed to the system. NO was obtained from a high pressure cylinder (Matheson gas) with the contents analyzing by I.R. about 2 mm Hg ($<0.3\%$) of NO_2 and the remainder NO ($>99\%$). Any appreciable NO_2 detected in the operation of the scrubber must necessarily have been produced by NO oxidation.

The scrubber was run under conditions similar to those in previous experiments except that both high and low temperatures were used. The resulting data are shown in Table VIII. The fact that the feed gas showed NO to NO_2 mole ratios similar to those experiments where N_2O_3 was used as the feed gas lends strong support to the idea that oxygen is being introduced to the system and is causing NO oxidation. The fact that the scrubber absorption efficiencies were quite low suggests that most of the oxidation is occurring in the infrared analysis cell after the gas passed through the scrubber, but there was still enough oxidation in the scrubber to cause up to 20% of the NO_x to be absorbed. The significant point is that a gas which analyzes more than 99.5% NO appears to have 30-50% NO_2 when it is fed to the scrubber system. Clearly some oxygen is entering the system and causing oxidation of the NO.

There is no apparent source of oxygen in the system, but only very small quantities of the gas would be necessary to explain the phenomena observed. It is possible that the gas moving at 40 ft/sec through the transfer lines in the scrubber feed system could be aspirating some air into the lines. Unfortunately, at the present time, it is impossible to analyze for low concentrations of oxygen, but a careful study is being made to determine possible sources of unwanted oxygen.

One might be tempted to conclude that the problem in the experiments discussed above is due to large errors in gas analysis. This would be reasonable except for the fact that the low material balance errors (5-10%) provide strong evidence that the gas analysis on the basis of total NO_x is correct. The material balance is obtained by comparing the amount of NO_x coming into the system with the feed gas (infrared gas analysis) with the total amount of NO_x leaving the system with the outlet gas (infrared gas analysis) and the outlet acid (analysis by titration with potassium permanganate). Thus, the low material balance errors are the result of two completely independent analytical techniques which suggests a high degree of precision in the measurements.

Table VIII. Operation of Scrubber Using Pure NO as Feed Steady State Operation*

	Run 27	Run 28
Inlet NO_2, ppm	2500	4000
Inlet NO, ppm	6100	4600
Outlet NO_2, ppm	3400	900
Outlet NO, ppm	3400	6300
Operating temperature, °F	75	250
Material balance error, %†	6.9	3.3
Gas side adsorption efficiency, %‡	19.1	15.7

Notes

* Acid flow = 100 cc/min, total gas flow = 20.0 ℓ/min, L/G = 4.0 mole/mole

$$\dagger\ \%\ \text{Material Balance Error} = \frac{\text{Inlet } NO_x \text{ (gas)} - \text{Outlet } NO_x \text{ (gas + acid)}}{\text{Inlet } NO_x \text{ (gas)}} \times 100$$

‡ Efficiency based on effluent gas and feed gas (infrared analysis).

The conclusion that can be drawn is that the gas analysis is correct in giving the total amount of NO_x entering and leaving the scrubber system, but it may very well be incorrect in giving the instantaneous proportions of NO and NO_2. To get this type of analysis, it is necessary to have rapid continuous monitoring equipment analyzing the gas streams. Continuous analysis is impossible with the infrared batch cell, but the new infrared (Beckman) and ultraviolet (DuPont) equipment make this type of inline analysis a routine task.

This discussion of the possible reasons for the variety of phenomena observed in the high temperature scrubber experiments should not be allowed to confuse the basic results of the testing. The high temperature scrubber does work at high efficiencies and the analytical data that verifies this conclusion are consistent and reproducible with material balance closure within 5-10%.

F. Summary of Results of High Temperature Scrubber Evaluation

Despite some experimental anomalies, it was shown reproducibly that mixtures of NO and NO_2 can be scrubbed with 80% sulfuric acid at high temperatures with high efficiency. The data obtained tend to reproduce and verify data obtained in earlier tests during the prior contract.

There is some evidence that it may not be necessary to have a precise 1:1 ratio of the two gases in order to obtain high absorption efficiencies at high temperatures. Continued work in this area would be necessary to determine any possible unforeseen absorption mechanism. This would be demonstrated in miniplant operation using gases more closely approximating flue gases.

V. VAPOR PRESSURE OF NITROGEN OXIDES OVER $HNSO_5/H_2SO_4$ SOLUTIONS

Although the vapor pressure of N_2O_3 over nitrose solutions has been investigated in the literature, considerable spread in data had been noted prior to this effort and no specific data were available in the high temperature regions critical to the Tyco process. The purpose of this subtask was to:

1. Review and evaluate the literature data for accuracy and reliability of method
2. Experimentally verify, if necessary, the available vapor pressure data of nitrogen oxides above $HNSO_5/H_2SO_4$ solutions in the area of H_2SO_4 strengths from 80 to 90% and temperatures of 250 to 350°F.

A. Literature Search

Many articles[5-20] relevant to the composition of nitrose solutions were found in our literature search. Most of the articles were not key source papers for actual vapor pressure data, but were merely supportive of various mechanisms outlined here and are footnoted at the appropriate locations in the text.

Key articles for vapor pressure data were those of A. N. Tseitlin and V. T. Yavorskii[20] and E. Berl and H. H. Saenger[5]:

1. Tseitlin and Yavorskii

The subject reference[20] describes a series of experiments in which the authors attempted to determine the partial pressure of nitrogen oxides over nitrose solutions in the original range of 56 to 84% H_2SO_4 with up to 33.6 wt % $HNSO_5$ added at temperatures of 122 to 194 °F by a dynamic gas flow method. Three thermostated sample vessels containing identical nitrose solutions prepared from known equimolar quantities of NO and NO_2 were equilibrated with a flowing stream of nitrogen. The flowing stream of nitrogen was scrubbed with concentrated sulfuric acid scrubbers which were assumed to remove the nitrogen oxides from the nitrogen gas stream. The scrubbers were then analyzed for nitrose content by a method not mentioned in the paper. The partial pressure of nitrogen oxides over the nitrose solutions were calculated from the calculated nitrose concentration of the scrubbers and the nitrogen flow rates.

Several conceptual and experimental flaws are evident in this work. In the first place, the authors neglect to mention the method of analysis of the scrubbers. Thus, one does not know whether a strong oxidant was used to titrate the scrubber contents or if a strong reducing agent such as mercury was used to convert the supposed $HNSO_5$ to NO. Secondly, the authors incorrectly assumed that concentrated sulfuric acid may be used to remove nitrogen oxides from a gas stream and dissolve them as $HNSO_5$. As shown later in this paper, at high sulfuric acid concentrations, $HNSO_5$ disproportionates to give NO_2^+ and NO. Thirdly, the authors prepared their solutions at constant ($NO + NO_2$) weight fractions and then attempted to derive an empirical equation relating all of their vapor pressure data. Since $NO + NO_2$ dissolves in H_2SO_4 to form $HNSO_5$ and H_2O, they would have achieved a better empirical correlation if they had used constant $HNSO_5$ concentrations at various H_2SO_4 concentrations. This is a result of the fact that the water content of nitrose solutions does not change if the solutions are made up with $HNSO_5$, but the water content of nitrose solutions increases for solutions made up with $NO + NO_2$. Fourthly, that the authors technique was inadequate to determine partial pressure of gases in equilibrium with nitrose solutions is confirmed by their incorrect values for the partial pressure of water.[19] Especially noteworthy is their value of 2.22 torr for the partial pressure of water above 81.25 wt % H_2SO_4 at 50 °C which they obtained, especially since other authors' data[1, 2, 3] lead one to expect a value less than 0.6 torr.

2. Berl and Saenger

These authors[5] used a batch method for obtaining vapor pressure data over nitrose solutions, similar to that which will be described in subsequent Tyco experimentation. Within their range of study, their data appear to be precise (0.1 mm Hg) internally consistent and consistent with other literatures[6, 7, 11, 12, 21] which have tended to be less precise. The vapor pressure data of Berl and Saenger can be treated to obtain the partial pressure of nitrogen oxides over nitrose solutions with acid concentrations in the range 64 to 80 wt % H_2SO_4. The total pressure above nitrose solutions containing 0 to 0.5M $HNSO_5$ was determined for the temperature range 30 to 150 °C for eight concentrations of H_2SO_4 in the range 64 to 80 wt % H_2SO_4.

Making the reasonable assumption that the partial pressure of nitrogen oxides is equal to the total observed pressure at a particular $HNSO_5$ concentration minus the total observed pressure at 0 $HNSO_5$ concentration and the same H_2SO_4 concentration and temperature, one may obtain the partial pressure of nitrogen oxides over nitrose solutions from their data. In addition, one may conclude that:

1. Henry's law may be used to describe the data. Thus, in Fig. 25, a Henry's law constant of 410 is obtained and the data correlate well with the calculated line.
2. One may extrapolate to higher temperatures by applying the relation $\log P = A + B/T$. Thus, in Fig. 26, a plot of log P versus reciprocal temperature is seen to be linear with $A = 5.286$ and $B = -1835$.

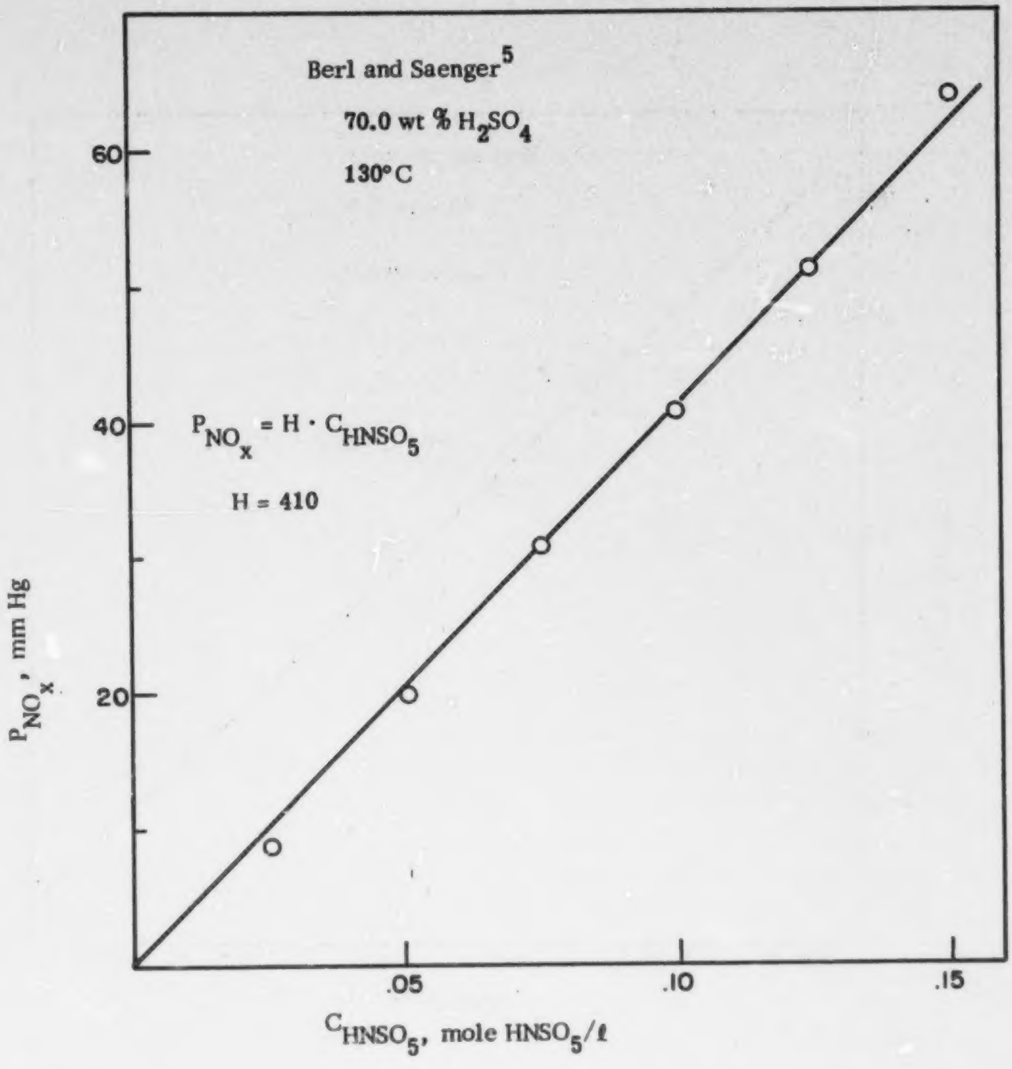


Fig. 25. Nitrogen oxide partial pressure, nitrosylsulfuric acid concentration dependence

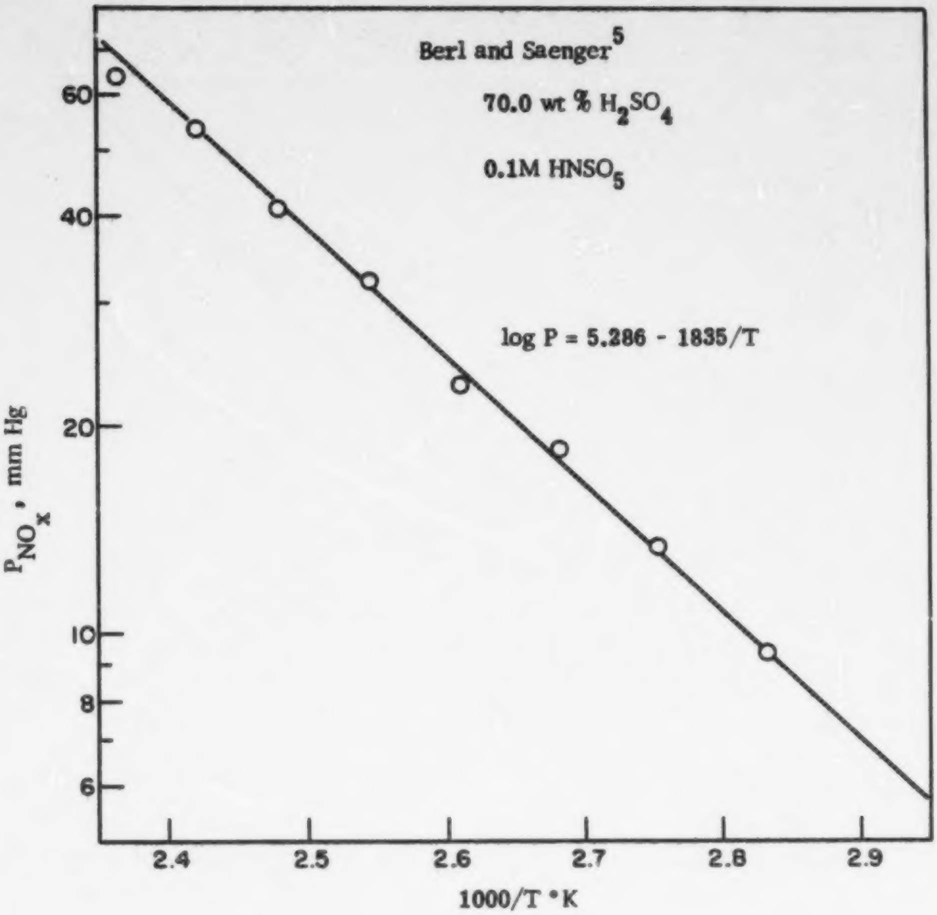


Fig. 26. Nitrogen oxide partial pressure, temperature dependence

3. At any given temperature and $HNSO_5$ concentration, the logarithm of the partial pressure of nitrogen oxides above nitrose solutions is a linear function of the H_2SO_4 wt %. For example, Fig. 27 verifies this for 0.1M $HNSO_5$ at 130 °C. Note that the partial pressure of nitrogen oxides above nitrose decreases as the sulfuric acid concentration increases.

B. Laboratory Work at Tyco

Work on the determination of the vapor pressure of nitrogen oxides over nitrosylsulfuric acid solutions entered the experimental stage after reexamination of the literature. The literature work supported the conclusion that there was no existing data available for nitrosylsulfuric acid solutions for acid concentrations above 80 wt % sulfuric acid or temperatures in the 250 to 350 °F range, although reasonable extrapolations might be made from Berl and Saenger at conditions close to their area of study.

1. Procedure

The experimental apparatus used at Tyco was similar to that of Berl and Saenger and is shown in Fig. 28. The solution to be examined was put into flask A, which was then cooled to about −20 °C. The entire system was then evacuated to a pressure of 1mm Hg. The flask was then tipped so that the acid manometer was partly filled with the acid solution thus forming a liquid seal between the flask A and the mercury manometer. The flasks and acid manometer were then put into an oven and connected (through a hole in the wall of the oven) to the rest of the system.

To measure the total vapor pressure of the system, the oven was slowly heated to a given temperature and held there. As the acid warmed and a pressure was created on the flask side of the acid manometer, the acid manometer became unbalanced. To offset this imbalance, argon was bled into the system on the other side of the acid manometer. The pressure of the mixed system outside the oven was measured with the mercury manometer. Thus, the pressure reading on the mercury manometer was equal to the total vapor pressure of the system in flask A. A series of readings could be obtained by increasing the temperature of the oven, holding it at each desired level until equilibrium was obtained. Equilibrium was assumed to have been attained when, for any given temperature, the mercury manometer pressure reading was constant for at least 15 min. One complete run gave the temperature dependence of the total vapor pressure of a solution containing a certain concentration of nitrosylsulfuric acid in sulfuric acid of a specific concentration.

2. Experimental results

The experimental data obtained at Tyco and some derived quantities are given in Tables IX through XIII and in Figs. 29 through 31. Table IX is a listing of data regarding the composition of the four nitrose solutions which we investigated. The strength of the sulfuric acid is expressed as the weight percent of H_2SO_4 in the solution prior to the addition of

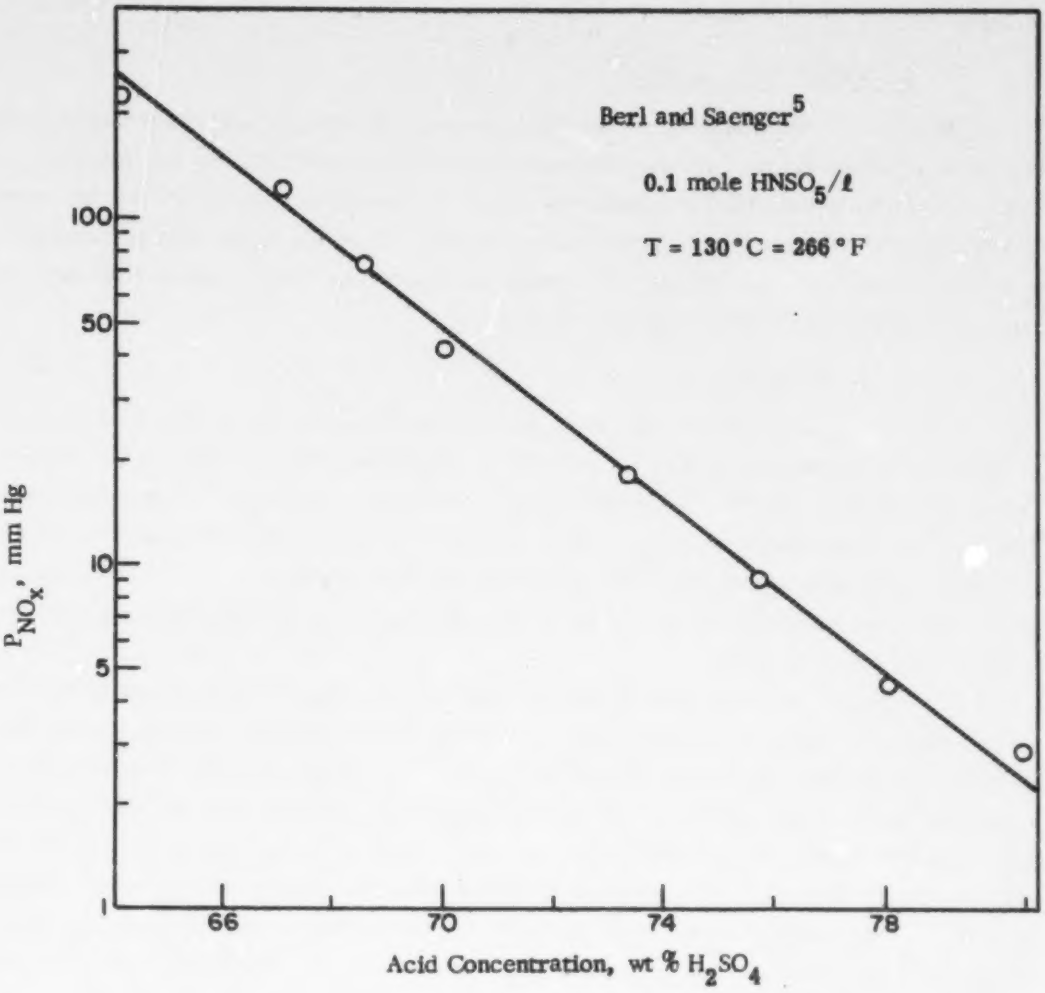


Fig. 27. Nitrogen oxide partial pressure, sulfuric acid concentration dependence

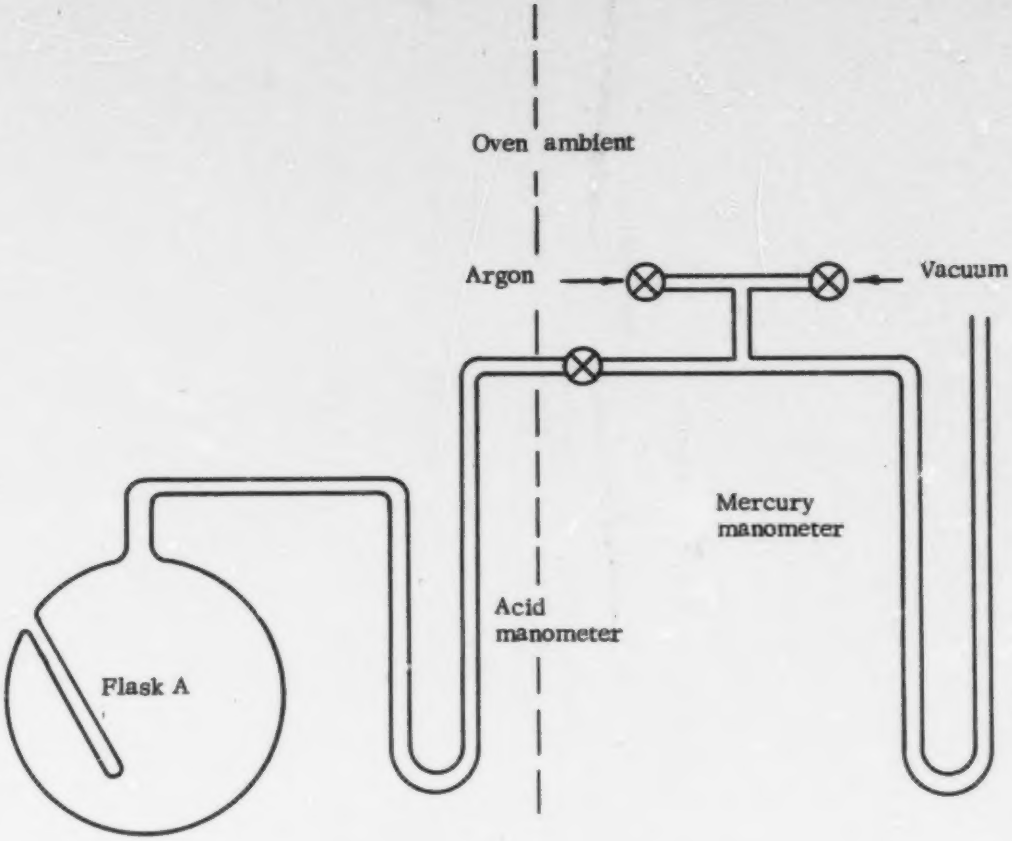

Oven ambient
Argon
Vacuum
Mercury manometer
Acid manometer
Flask A

Fig. 28. N_2O_3 vapor pressure analysis apparatus

Table IX. Tyco Sample Compositions

	Experimental Data		Derived Quantities			
Specific Gravity	0.1N $KMnO_4$/10 ml sample, ml	NO/ml sample, ml	$HNSO_5$ Molarity Assuming Oxidation State = 3	Calculated Oxidation State	Calculated $HNSO_5$, mol/ℓ	Calculated NO_2^+, mol/ℓ
1.74	18.8	—	0.093	—	—	—
1.77	19.2	2.4 @ 25 °C	0.096	3.04 ± 0.1	0.096	0.002
1.815	18.5	—	0.096	—	—	—
1.84	18.8	2.7 @ 24 °C	0.094	3.31 ± 0.08	0.094	0.017

Table X. Tyco Vapor Pressure Data for 80.08 wt % H_2SO_4 *

Temperature, °C	Observed Pressure, torr	Calculated Pressure (torr), Corrected to 0.1 mol/ℓ $HNSO_5$
61.7	3	3
76.7	7	7
98.9	16	16
115.6	35	36
132.2	69	71
144.4	113	116
165.6	184	190

---

*0.097 mole $HNSO_5$/ℓ.

Table XI. Tyco Vapor Pressure Data for 84.04 wt % H_2SO_4 *

Temperature, °C	Observed Pressure, torr	Calculated Pressure (torr), 0.1 mol/ℓ
70	2	2
85	6	6
115.5	20	20
133	38	39
155	93	95
163	145	148

---

*0.098 mole $HNSO_5$/ℓ.

Table XII. Tyco Vapor Pressure Data for 90.16 wt % H_2SO_4*

Temperature, °C	Observed Pressure, torr	Calculated Pressure (torr), 0.1 mol/ℓ
57	1	1
82	3	3
102	6	6
127	20	21
144	35	36
162	60	63

---

*0.096 mole $HNSO_5$/ℓ.

Table XIII. Tyco Vapor Pressure Data for 95.0 wt % H_2SO_4*

Temperature, °C	Observed Pressure, torr	Calculated Pressure (torr), 0.1 mol/ℓ
70	1	1
86	2	2
120	8	9
131	13	14
141	18	19
158	25	27
166	39	41

---

*0.094 mole $HNSO_5$/ℓ.

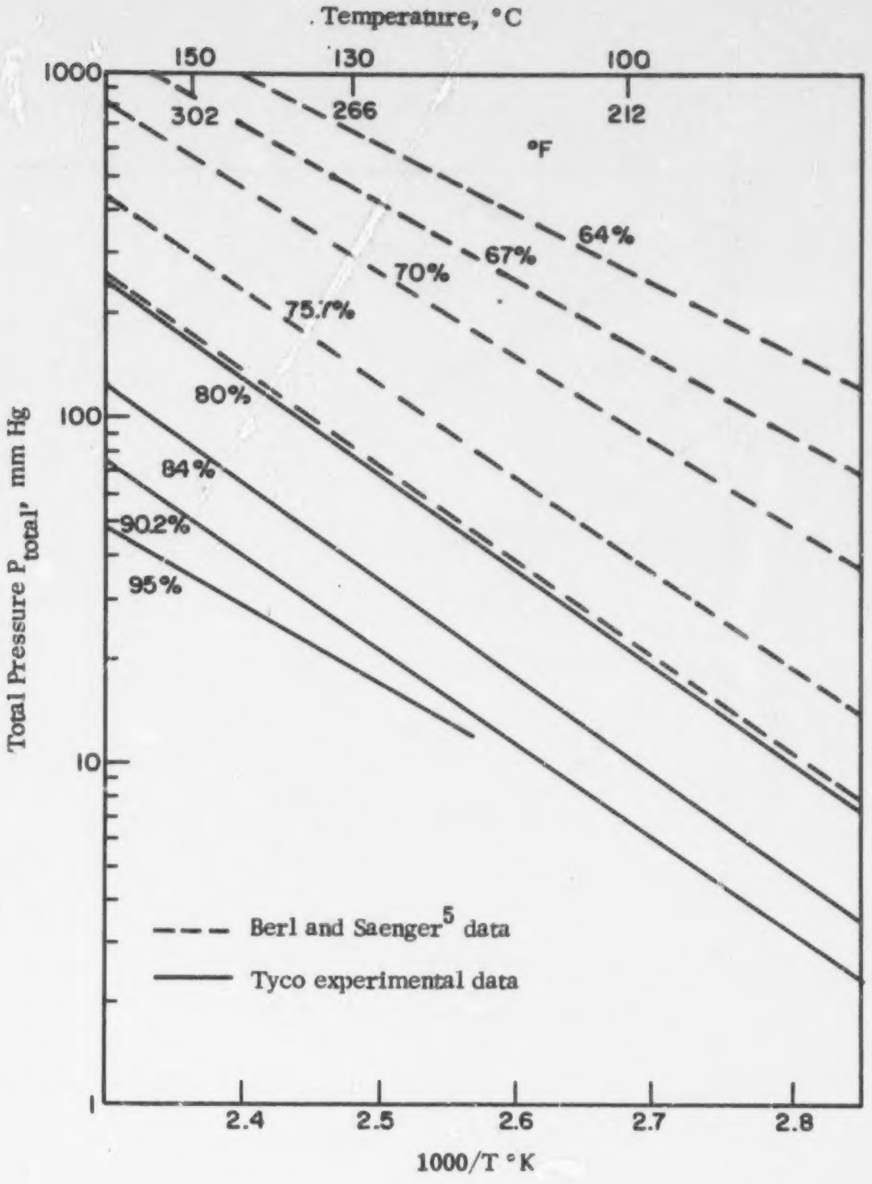


Fig. 29. Total vapor pressure over nitrose solutions containing 0.1M $HNSO_5$

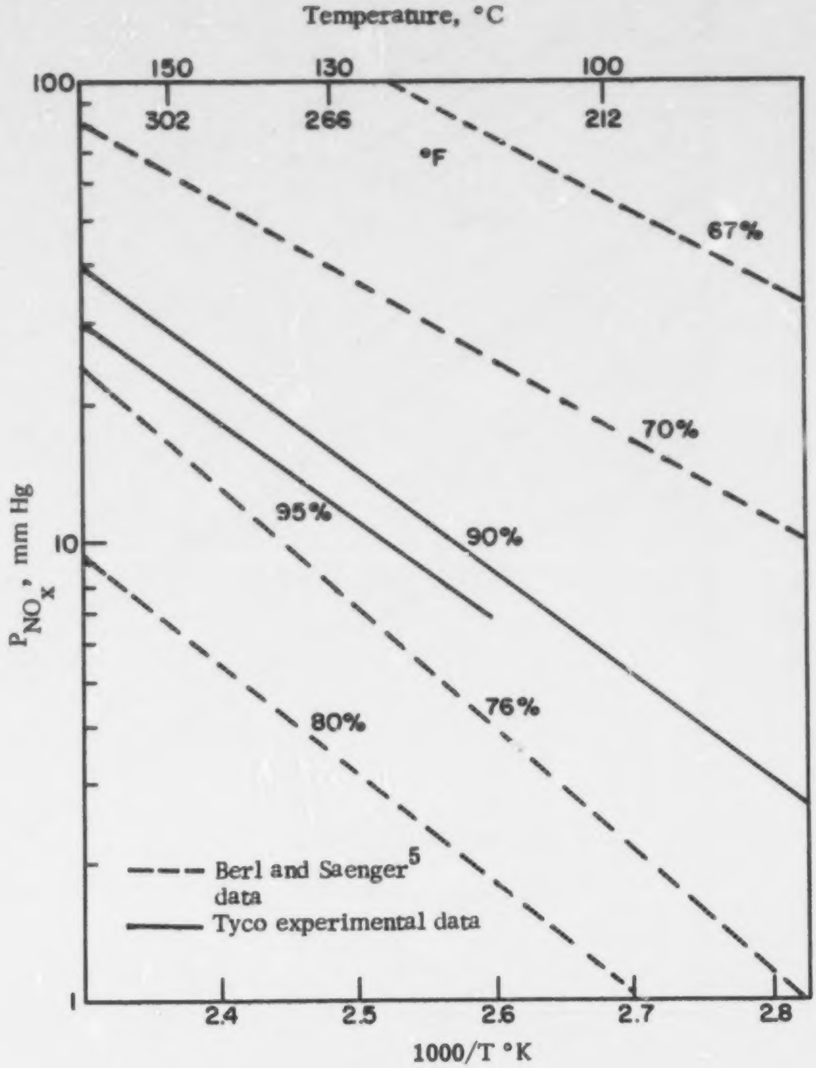


Fig. 30. Nitrogen oxide partial pressures over nitrose solutions containing 0.1M $HNSO_5$

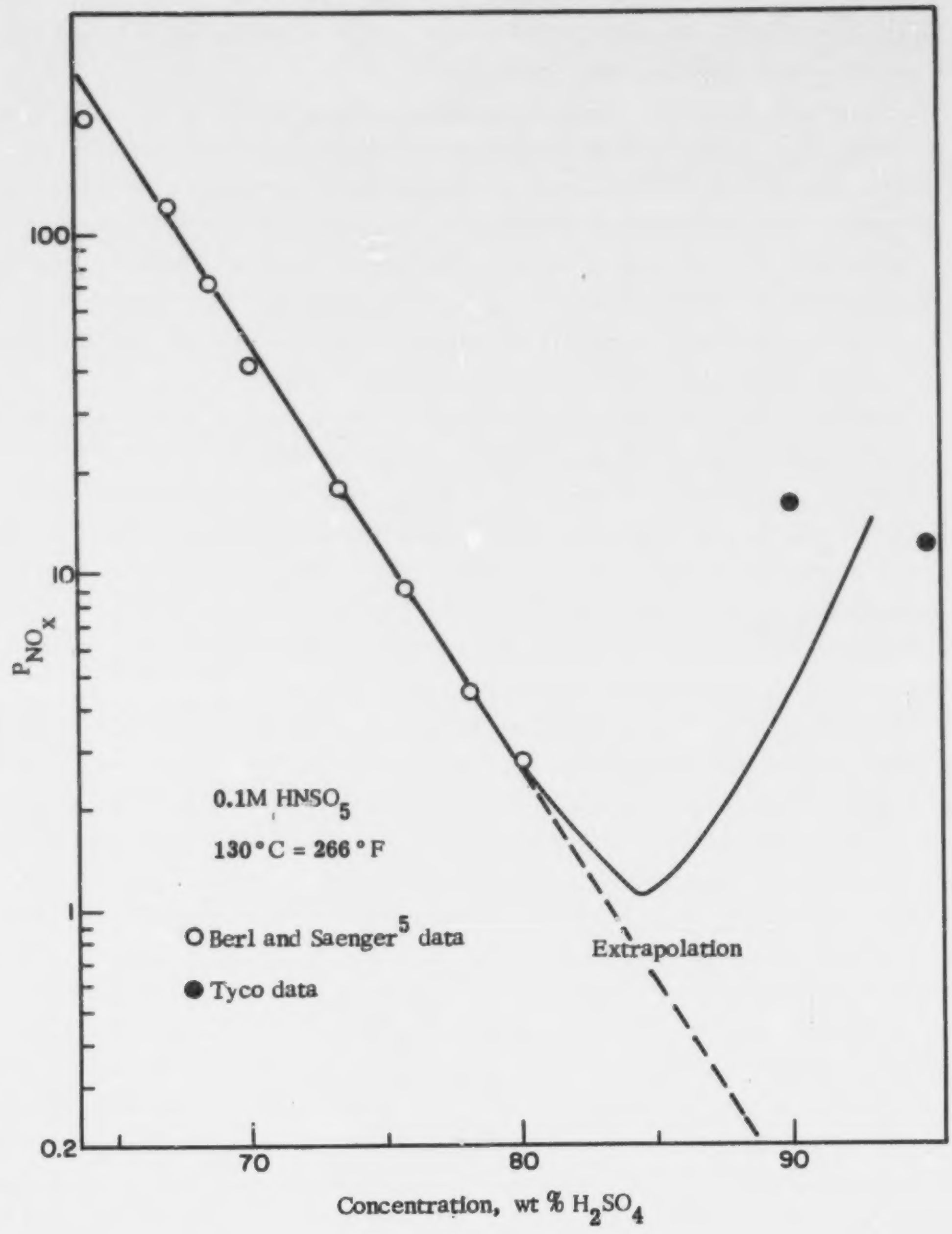


Fig. 31. Nitrogen oxide partial pressure over nitrose solutions. Concentration dependence – experimental values

the $HNSO_5$. The original analytical data for $HNSO_5$ analysis are given in columns 3 and 4 so that future investigators may have access to experimental quantities rather than derived functions. The later columns refer to derived results.

If a sample is known to contain all dissolved nitrogen as $HNSO_5$, the concentration of the $HNSO_5$ may be determined by permanganate titration or with a nitrometer. In the case of the permanganate titration, the $HNSO_5$ is oxidized to HNO_3 which is an oxidation state change of two. Thus, for each two equivalents of $KMnO_4$ required to titrate the sample, there is 1 mol of $HNSO_5$ present. In the case of the nitrometer, all of the $HNSO_5$ is reduced to NO and one measures the volume of NO formed to determine the total number of moles of $HNSO_5$ present. The permanganate titration is more precise and faster than the nitrometer determination and is thus normally used to the exclusion of the nitrometer.

If one has reason to suspect that the nitrogen may be present as other than $HNSO_5$, it is necessary to perform both analyses. We know from the literature[8, 9, 10, 11, 12, 14, 15, 18, 21] that, at acid concentrations less than 65 wt % H_2SO_4, the $HNSO_5$ disproportionates to form HNO_3 and NO thereby causing the mean oxidation state of the dissolved nitrogen species to be greater than three and less than five. The nitronium ion, NO_2^+, is a well characterized oxidizing agent (nitrogen oxidation state of 5) which is stable in concentrated sulfuric acid[9, 10] exceeding 84 wt % H_2SO_4. We thus had reason to expect that at sufficiently high concentrations of sulfuric acid, the $HNSO_5$ might disproportionate to NO_2^+ and NO.

The oxidation state of the dissolved nitrogen species is calculated as follows: (1) the permanganate titration is performed to oxidize all of the nitrogen species to the +5 oxidation state thereby giving the number of equivalents required to do this, and (2) the nitrometer is used to reduce all of the nitrogen species to NO, thereby giving the total number of moles of nitrogen species. Dividing the number of equivalents by the number of moles gives the oxidation state change experienced during the permanganate oxidation. Subtracting this from five gives the mean oxidation state of the dissolved species. As an example, consider the 95.0 wt % H_2SO_4 sample. In this case, 18.8 ml of 0.100N $KMnO_4$ were required to titrate 10 ml of sample. This is equivalent to 0.188 equivalents of $KMnO_4$ per liter of sample. In the nitrometer run, 2.7 ml of NO were produced from a 1 ml sample at 24 °C at which temperature the molar volume of an ideal gas is 24.37 ℓ/mol. This corresponds to 0.1108 mol of NO per liter of sample. Dividing 0.187 equivalents/ℓ by 0.1108 mol/ℓ, one obtains an oxidation state change of 1.69 ± 0.08 equivalents/mol. Subtracting this from 5.00 one obtains an oxidation state of 3.31 ± 0.08. This, in turn, leads to calculated concentrations of 0.094M $HNSO_5$ and 0.017M NO_2^+ at 24 °C. Since we are postulating that the NO_2^+ is formed by disproportionation of $HNSO_5$, viz:

$$3\ HNSO_5 \rightarrow 2\ NO + NO_2^+ + HSO_4^- + H_2S_2O_7,$$

we know that 2 mol of NO are formed per mole of NO_2^+, and thus in this case 0.034 mol of NO went into the gas phase for each liter of solution at 24 °C. We will come back to this conclusion in our subsequent interpretation of data (see Section V.C).

Tables X through XIII list the experimental vapor pressure data. The total observed pressure data, corrected to 0.100M $HNSO_5$ using Henry's law, are plotted in Fig. 29 both for the Berl and Saenger and the Tyco data. The Tyco 80.08 wt % H_2SO_4 data fall close to but slightly below the Berl and Saenger 80.02 wt % H_2SO_4 data indicating that we are in substantial agreement. Due probably to the large volume (500 ml) of our solution and the fact that we did not stir this solution, we believe that our observed pressure values may be slightly less than the equilibrium values. Nevertheless our values are close enough to those of Berl and Saenger[5] to indicate agreement. We have thus confirmed the reliability of the Berl and Saenger[5] method.

C. Interpretation of Tyco Results

Fig. 29 demonstrates that the curves for our higher acid concentrations lie progressively lower than the 80% curve, as expected. For our 90.16 wt % H_2SO_4 and 95.0 wt % H_2SO_4 data, the observed total pressures are substantially higher than the approximate values of water vapor pressure which may be obtained from the data of Greenewalt.[7] Thus, since the correction term for water vapor pressure is small, it is possible to calculate the partial pressure of nitrogen oxides with a low percentage error. Note that in Fig. 30 the partial pressure of nitrogen oxides for 90.16 and 95.0 wt % H_2SO_4 are higher than for 80.02 wt % H_2SO_4. This is in contrast to the trend noted by Berl and Saenger at lower concentrations of H_2SO_4 for which the partial pressure of nitrogen oxides was observed to decrease steadily as the sulfuric acid concentrations increased. We contend that this is due principally to the formation of NO by disproportionation of $HNSO_5$ as outlined earlier. Since the samples were degassed prior to vapor pressure measurements by cycle of pumping with a mechanical vacuum pump while frozen at dry ice-acetone temperatures followed by thawing, all of the NO formed at room temperature was lost and the high observed pressures at higher temperatures must have been due to a positive temperature coefficient for the disproportionation reaction.

Fig. 31 is a plot of partial pressure of nitrogen oxides above nitrose solutions (0.1M $HNSO_5$) at 130 °C versus H_2SO_4 concentration. Note that data for the 64 to 80 wt % H_2SO_4 if extrapolated to higher acid concentrations indicate that the partial pressure of nitrogen oxides would be quite low at all acid concentrations above 80%. However, our data for 90 and 95% acid indicate that the disproportionation of $HNSO_5$ occurs at these concentrations. It is important to determine just where in the 80 to 90% range this disproportionation reaction becomes important. At acid concentrations below 84%, the H_2O/H_2SO_4 mol ratio is greater than one and the activity of water (which could act to destabilize NO_2^+) is much higher than at acid concentrations higher than 84%.[6] We thus have reason to believe that, since $HNSO_5$ disproportionation depends in part on stabilization of NO_2^+, this disproportionation reaction will become important when the sulfuric acid concentration exceeds 84%.

VI. LABORATORY SCALE MINIPLANT - MODIFICATION AND EXPERIMENTATION

A. Goals of Miniplant Operation

1. Conceptual goals

The research work during the 2 1/2 years preceding the operation of the miniplant had been successfully devoted to the conceptual and experimental development of a process which could remove the oxides of sulfur and nitrogen from power plant flue gas. The resultant process includes major modifications of the century-old process on which it is based and these new process stages require extensive experimental characterization and verification before large scale operations can be attempted.

Experimental work on the separate process stages during the latter phases of the previous contract and the early stages of this contract gave ample evidence that the process was very promising, but there was the definite need to demonstrate that the individual stages could be put together and made to work as an integrated unit. Thus, one of the major goals of the miniplant operation was to provide a more comprehensive experimental verification of the viability of the Tyco Catalytic Chamber Process.

2. Scale-up goals

After experimental verification of the process concept, the long range goal is to design, construct and operate a full scale plant in conjunction with an industrial power plant. In working toward this goal, it will be necessary to scale up in stages, with each stage being used to develop engineering data to permit design of the next size plant.

Toward this end, the miniplant is to be used to determine a range of operating characteristics of the major process stages to permit scale-up to pilot plant level. Thus, by the time the miniplant evaluation period is completed, it should be possible to design a pilot plant that will permit the optimization of the process so that full scale plants can be built.

3. Evaluation of the major process stages

Although there are a great many aspects of the process that must be optimized, the work can be broken down into the characterization of the three main process units: (1) the reactor, (2) the scrubber, and (3) the stripper. Proper optimization of these stages will require a complete parametric study of the process operation, and this will have to be done before the industrial scale pilot plant is designed and built. The goals of this contract were limited to the verification of the feasibility of the important process stages and the determination of the order of magnitude of some of the key operating variables. Some of the significant variables examined in this manner were:

Preceding page blank

Reactor:	Operating temperature range Residence time
Scrubber -	Scrubbing efficiency Number of equivalent scrubbing plates Height of a theoretical plate
Stripper -	Operating temperature range Stripping efficiency Residence time Bed depth

B. Miniplant Modification

1. Background

At the start of this contract, the miniplant was in operational condition for evaluating a process concept that preceeded the development of the catalytic stripper. The plant consisted of a reactor, a low temperature scrubber, a hot air stripper (packed with ceramic saddles) and an acid concentrator. With the change in process concept, the acid concentrator was no longer needed and the scrubber and stripper had to be extensively modified. Much of the equipment needed for the required modifications was made available by salvaging parts of the old equipment, but some new items were needed. Details of this are given in the following sections of this report.

2. Flowsheet

The flowsheet for the modified miniplant is shown in Fig. 32. The plant is set up so that each stage could be isolated and the effluent stream either analyzed or dumped. There is a bypass to the stack between the reactor and the scrubber so that the flue gas could be contacted with oxides of nitrogen and brought to steady state before being fed to the scrubber. This avoids the problem of diluting or concentrating the acid while the scrubber is being heated to its operating temperature. Most of the bypass lines were equipped with condensers to avoid venting wet gas streams, which would cause acid condensation in the vent fan. The flowsheet also shows the location of the sample ports leading to the analytical system which will be discussed in detail below.

3. Reactor

The SO_2 oxidation reactor was not altered from its earlier design since its function had not changed. It consisted of about 57 in. of 4-in.-diameter pipe (volume: 0.414 ft^3) with a thermometer well mounted in the middle. (See Fig. 33). Originally the reactor had two heating mantles on it, each 12 in. long. To these were added heating tapes so that the entire length of the reactor was heated. The heating tapes and exposed portions of the tube were insulated with aluminum-foil backed fiberglass insulation. At various times, different baffles were placed between the flanges at the joints to create turbulence to enhance mixing and the chamber was so designed that these could be replaced or removed very quickly without shutting down the operation of the plant. The residence time of the gas in the reactor at a flow rate of 10 SCFM (14.4 ACFM at 250°F) is 1.7 sec.

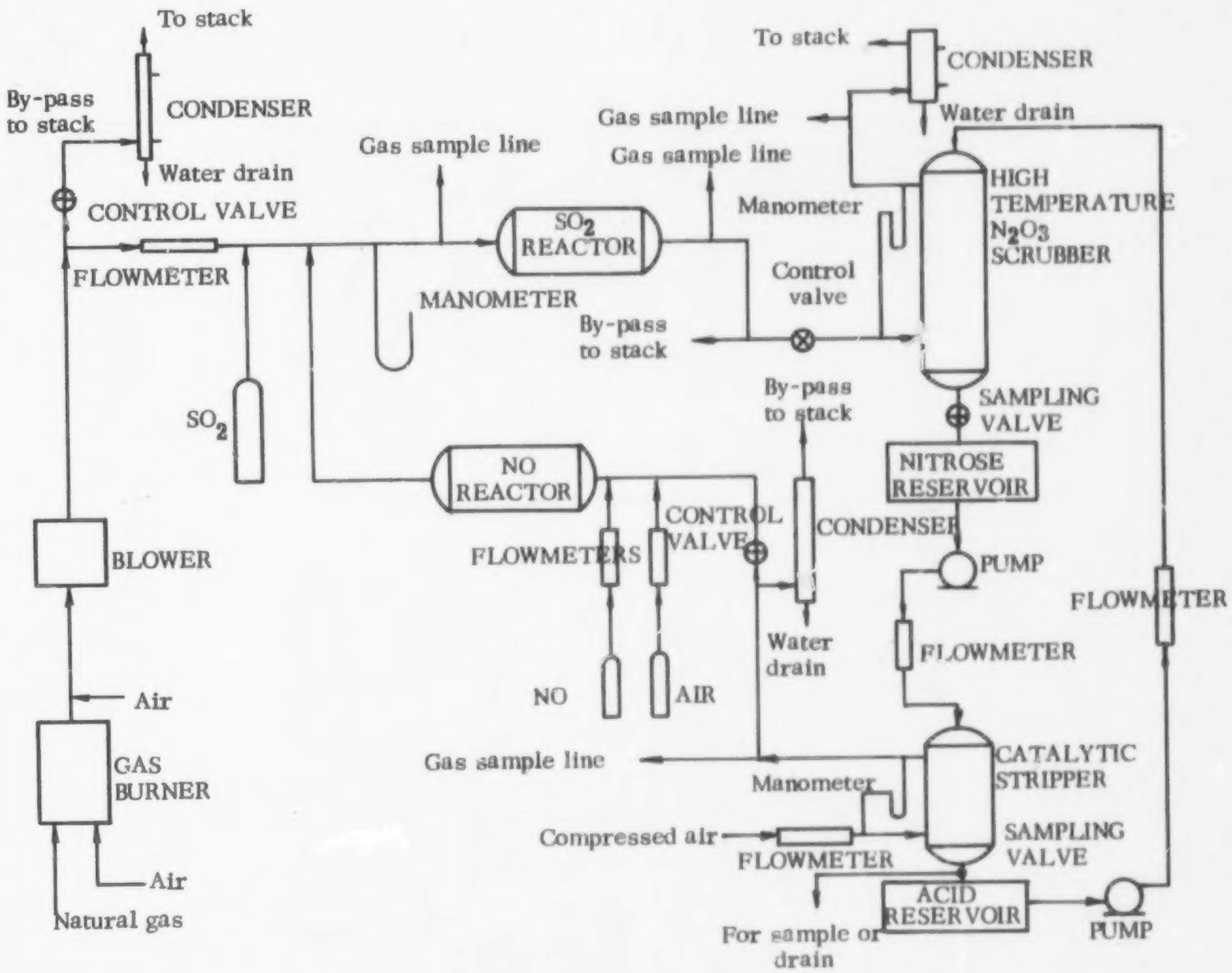

To stack
By-pass to stack
CONDENSER
Water drain
CONTROL VALVE
FLOWMETER
BLOWER
Air
GAS BURNER
Air
Natural gas
SO_2
Gas sample line
MANOMETER
SO_2 REACTOR
NO REACTOR
Gas sample line
To stack
CONDENSER
Gas sample line
Water drain
Manometer
HIGH TEMPERATURE N_2O_3 SCRUBBER
Control valve
By-pass to stack
By-pass to stack
SAMPLING VALVE
NITROSE RESERVOIR
CONTROL VALVE
CONDENSER
FLOWMETERS
PUMP
FLOWMETER
FLOWMETER
Water drain
NO
AIR
Gas sample line
CATALYTIC STRIPPER
Manometer
Compressed air
FLOWMETER
SAMPLING VALVE
ACID RESERVOIR
PUMP
For sample or drain

Fig. 32. Miniplant flowsheet

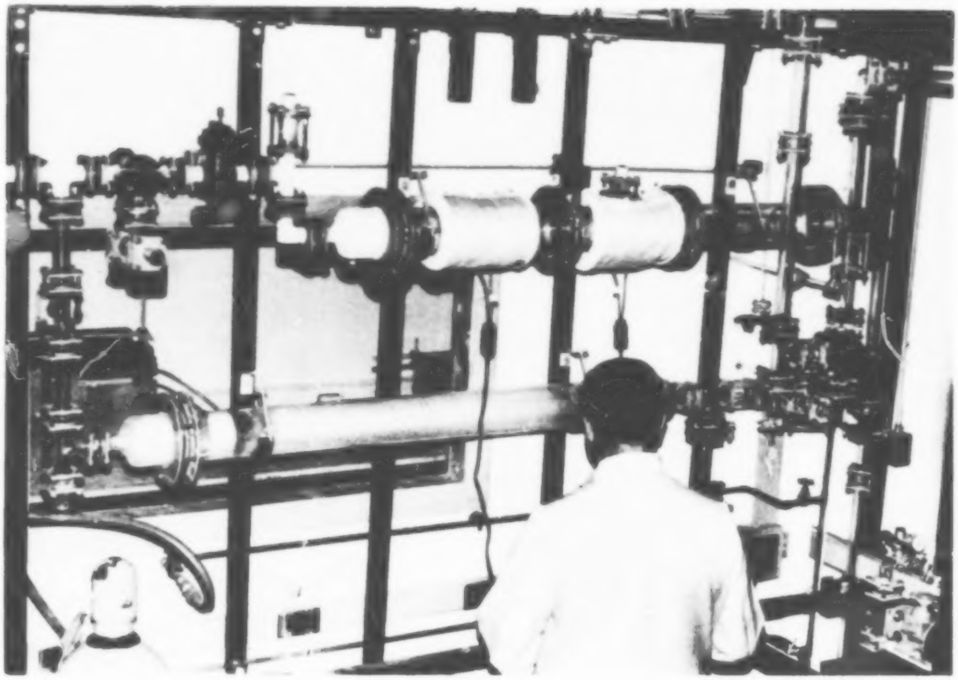


Fig. 33. Miniplant showing SO_2 reactor (above) and NO oxidizer. (This photo was taken before the heating tapes and insulation were put on.)

4. High temperature scrubber

The high temperature scrubber and the original low temperature scrubber had essentially the same purpose, i.e., to remove the sulfuric acid mist from the gas stream and to recover the oxides of nitrogen. No modifications were made to the 4-in.-diameter packed scrubber (Fig. 34) other than to equip the column with heaters so it could be operated at the desired temperatures.

For heating, the column was provided with four heating mantles and several heating tapes with the entire length being insulated. The heating elements were ganged into two units so that temperature control could be accomplished by two-zone heating. A thermometer well was located half way up the column. In addition, there were thermometer wells located so that the temperature of all inlet and outlet streams could be monitored.

The packing remained as 3/8-in. ceramic Intalox saddles packed to a height of 8.5 ft. Several redistributors were placed in the column to prevent channeling through the column. A manometer was installed so that the pressure drop across the scrubber could be determined and isolated from the rest of the gas loop (see Fig. 32).

A reservoir was provided at the base of the column so that there would be a constant source of liquid for the stripper feed pump. An acid sample port was provided before the reservoir.

5. Catalytic stripper

The stripper column (4-in. diameter by 6 ft. high) consisted of four beds, each containing 2 in. of saddles supporting 8 in. of Witco type 256 activated carbon. (See Fig. 34). The saddles were used to prevent the relatively fine carbon particles from falling through the holes in the glass support plate. One redistributor was installed half way down the column. There was an acid reservoir and sampling port at the bottom of the column. The column was also equipped with a manometer to determine the pressure drop.

The column was equipped with heating mantles and heating tapes so that the stripper could be heated to temperatures up to about 300°F. Three thermometer wells were installed so that the temperature could be measured at various heights in the column. Again, there were provisions for measuring the temperature of all inlet and outlet streams.

The stripper was fed with acid from the bottom of the scrubber and air from a compressed air line. Both lines had flowmeters so that flow rates could be monitored. The effluent acid was pumped back to the scrubber while the effluent gas was either recycled to the reactor or vented to the stack. Samples could be obtained of all input and output streams.

6. Nitrogen oxide feed

At startup, the NO_2 needed for feed to the SO_2 oxidation reactor is provided by air oxidation of bottled nitric oxide. As shown in Fig. 32, the NO and air (from a compressed air source) are fed to a pipe reactor which allows about 45 sec residence time at a flow rate of about 0.3 SCFM. This should be sufficient to provide 90% oxidation of NO to NO_2 under conditions necessary to provide 7000 ppm of NO_2 to a 10 SCFM gas stream.

If the miniplant is running at steady state and the stripper is providing sufficient NO_x for recycle, the bottled NO is turned off and the stripper effluent gas is piped into the SO_2 reactor through the NO oxidizer. The NO oxidation reactor was wrapped with heating

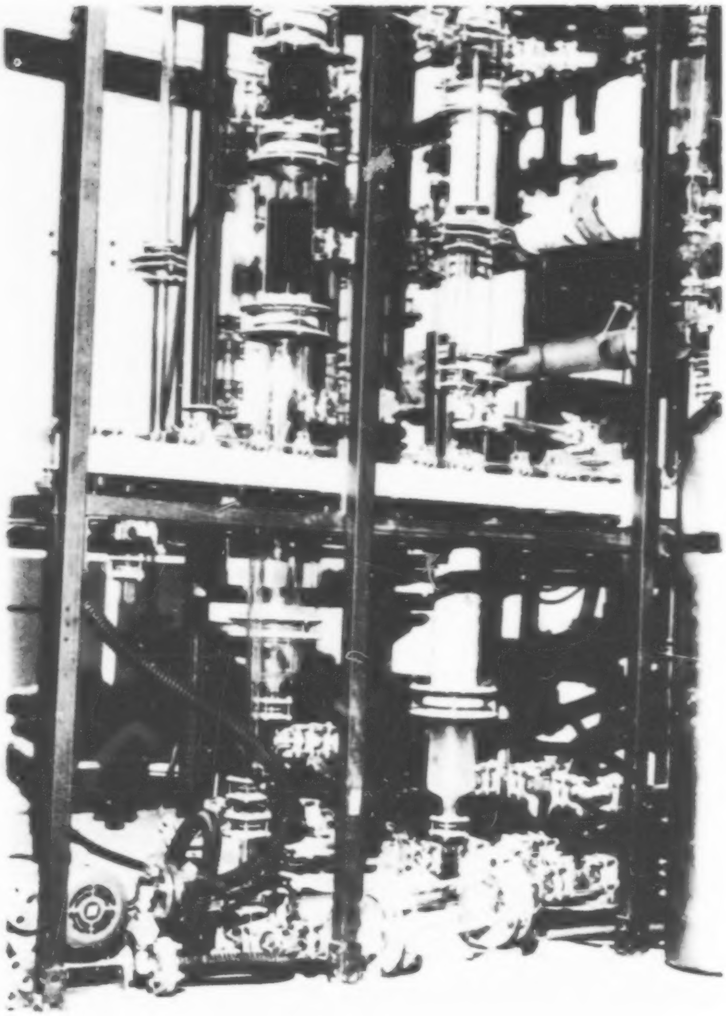


Fig. 34. Miniplant showing stripper (left) and scrubber columns (this photo was taken before the heating mantles, heating tapes and insulation were put on)

tapes so that the recycled gases from the stripper could be kept hot to avoid water condensation. When used as a chamber for NO oxidation, the heaters are turned off since this oxidation reactions occurs with higher rates at low temperatures.

7. Fluid flows - pumps and blower

The miniplant was originally designed for a flue gas input flow of 10 SCFM. All other flow rates were calculated based on the gas flow rate, using theoretical considerations and laboratory data to size fluid handling equipment.

The acid flow rate in the scrubber/stripper loop was based on an L/G ratio of 2.5 mole/mole in the scrubber as determined in the previous contract. Recommendations by TVA and Tyco Lab experiments revealed a scrubber L/G ratio of about 4.6 mole/mole to be more feasible. The original pumps had a maximum flow rate of 0.2 gpm, with 0.39 gpm required for an L/G of 4.6 mole/mole. In view of delivery time limitations on the high temperature corrosion resistant positive displacement pumps, it was decided to perform the miniplant scrubber experiments at maximum pumping rates and modify gas flow rates accordingly for scrubber operation (~5 SCFM). Three pumps were available for the scrubber/stripper loop with two for continuous operation, and one as a spare.

The laboratory scale stripper utilized an L/G of 16 lb/lb in most of the experimentation, and it was decided to use this order of magnitude in the miniplant stripper. With 80% acid being fed at 0.14 gpm, compressed air feed of 2 SCFM was used giving an L/G of approximately 13.

C. Analytical Instrumentation and Sampling Procedures

1. Background

During the previous contract (No. PH 86-68-75), gas analysis had been performed using two spectrophotometric methods: (1) infrared and (2) ultraviolet photometric analysis. The ultraviolet method was quite satisfactory for analysis of NO_2 and SO_2, but the particular setup was not very sensitive and it could not be used to analyze for NO. The infrared system was more sensitive and could be used for NO, NO_2 and SO_2 analysis, but it could only be operated on a batch sampling basis which made it impossible to do NO and NO_2 balances since by the time the batch test was run, the NO would have oxidized to NO_2. Water interference in the IR, while overcome by scrubbing or cold traps, limits the flexibility of this method.

2. Inline continuous analytical monitoring

For the continuous miniplant operation, it was necessary to obtain suitable instrumentation that could be used on an inline, continuous basis. After extensive discussions and examination of industrially available instrumentation, Tyco decided to purchase two instruments which appeared to be well suited to the task at hand. These instruments are:

1. DuPont Model 400 Ultraviolet Photometer: This instrument has been used by TVA for analysis of SO_2 in laboratory and pilot plant applications. The model purchased by Tyco is capable of monitoring SO_2 and NO_2 sequentially using the attenuation of ultraviolet radiation at two specific wave lengths. The major advantage of this instrument over other commercially available analyzers is that the sample can be maintained at very

high temperatures which is very important when working with a gas stream that contains very high concentrations of water which would condense out at the operating range of many of the other available instruments (usually around 125°F maximum).

2. Beckman Model 315A Infrared Analyzer: This device is used to measure the concentration of NO in the sample gas streams. As with all infrared photometers, it is very sensitive to the water content of the gas stream since the infrared absorption band for water overlaps the absorption band for NO. For this reason, the gas stream was first passed through the DuPont analyzer and then through a condenser trap so that the water could be removed before sending the gas into the IR analyzer chamber.

Both instruments were equipped with dual sensitivity ranges so that both high and low gas concentrations could be measured. The concentration ranges of the two instruments are:

NO_2	0 - 10,000 ppm (by volume)
	0 - 1,000
SO_2	0 - 5,000
	0 - 500
NO	0 - 5,000
	0 - 1,000

A photograph of the instruments is shown in Fig. 35.

3. Miniplant gas sampling

It was necessary to analyze the gas streams at four points in the system:

1. Inlet gas after the introduction of SO_2 and recycle NO_2
2. Reacted gas just after the reaction chamber
3. Stack gas just after the scrubber
4. Recycle NO_2 stream just after the stripper.

Gas samples were removed from the system at these four points and conducted to the analytical instrumentation through 1/4-in. glass pipe which was heated to prevent condensation. Fig. 36 shows a schematic diagram of the gas sampling and instrumental analysis system.

The procedure for gas analysis is to flow the gas from the desired sample port through the sample lines into the DuPont analyzer and obtain sequential NO_2 and SO_2 concentration values, while simultaneously reading the NO concentration obtained on the Beckman analyzer. Then a sample would be taken from another sample port and the procedure repeated. This procedure obviously depends on being able to equilibrate the instruments for a particular gas sample in a reasonably short time. In practice, rapid scanning of the various sample ports was very difficult to achieve, as will be discussed later in the section on experimental results.

D. Experimental Results

1. Plant start-up

The start-up of the miniplant actually was accomplished in two phases: (1) instrument calibration and evaluation, and (2) miniplant operation. (See Appendix III for startup procedures.) The first phase, which was carried out at the same time as the overall performance evaluation, lasted about 1 week and permitted operating personnel to become acquainted with the characteristics of both the instruments and the plant equipment. Operation of the miniplant continued for the next 2-week period.

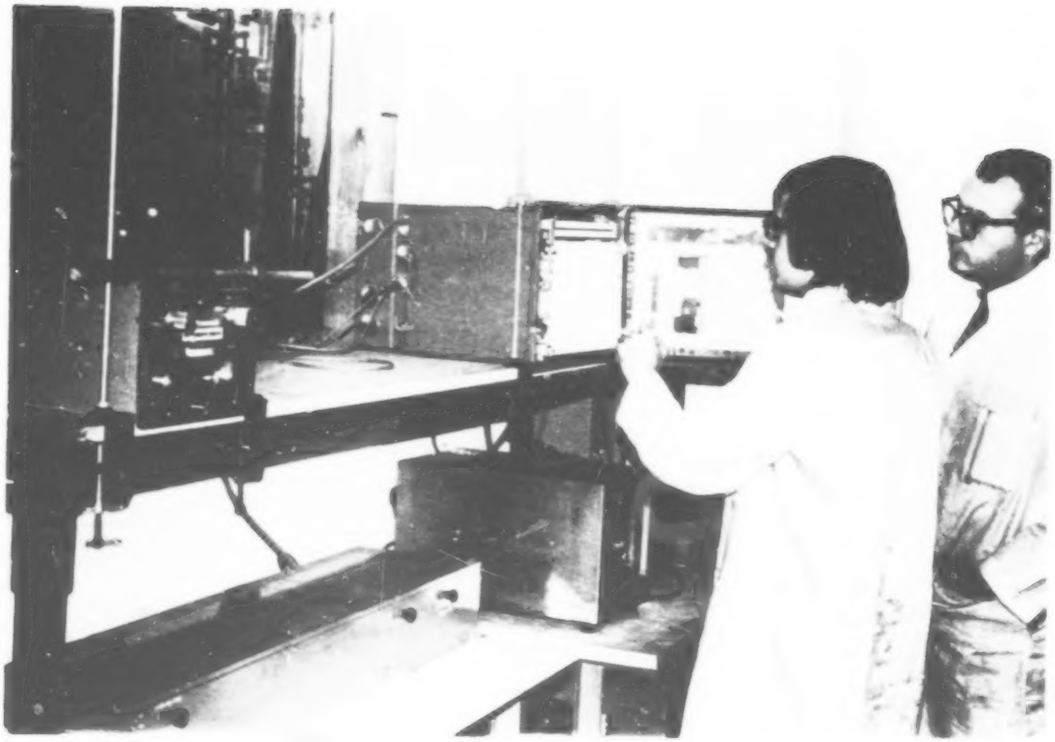


Fig. 35. Miniplant analytical instrumentation

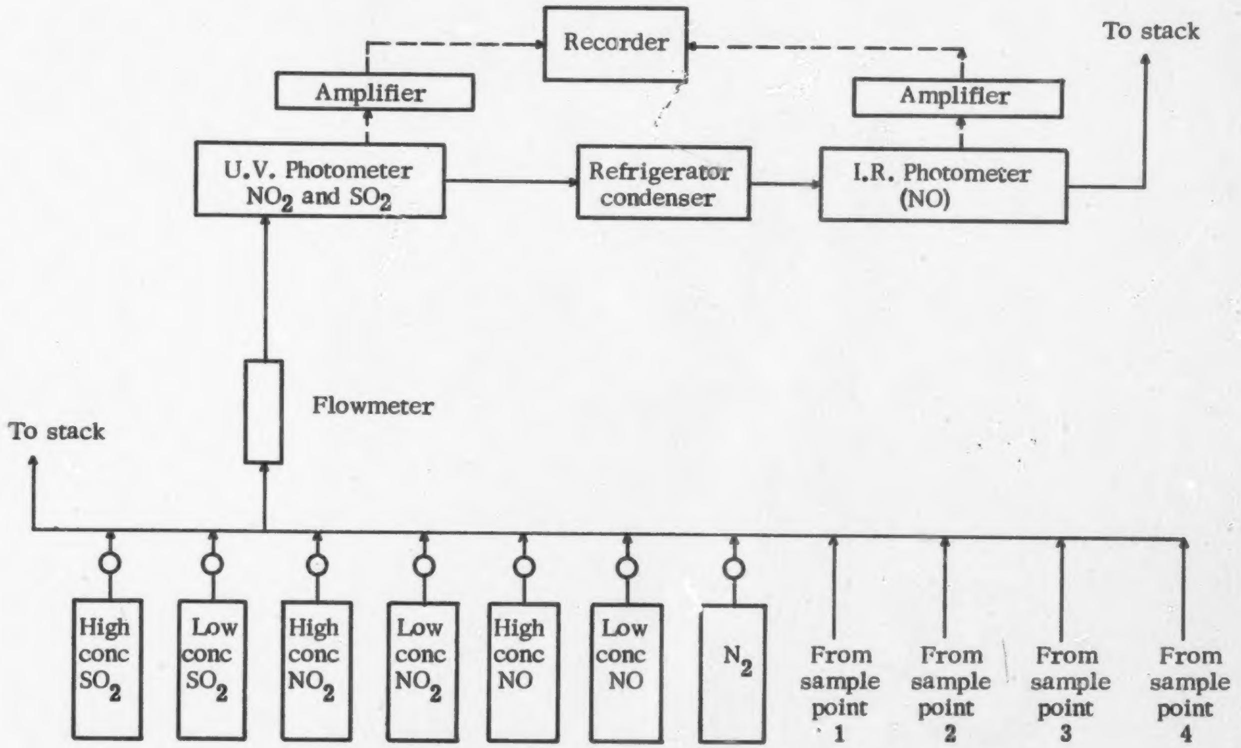

Recorder
Amplifier
Amplifier
To stack
U.V. Photometer NO_2 and SO_2
Refrigerator condenser
I.R. Photometer (NO)
Flowmeter
To stack
High conc SO_2
Low conc SO_2
High conc NO_2
Low conc NO_2
High conc NO
Low conc NO
N_2
From sample point 1
From sample point 2
From sample point 3
From sample point 4

Fig. 36. Gas sampling and analysis system

2. Instrument evaluation

Electronic calibration of the DuPont and Beckman spectrophotometers was quite straightforward and was accomplished in a short period of time. However, due to the variety of gas sample sources, calibration and use of the instruments to analyze gas streams was more involved and took more time to get used to.

A major consideration in operating the instruments is that the measurements must be made at constant temperature and pressure in the sample chamber or else corrections must be made. This is because the instruments do not really measure concentration but the absolute number of molecules in the radiation beam. Thus the machine would give the same reading for two gases, one of which had twice the actual concentration (of SO_2, for example) as the other, but was read at one half the absolute pressure. In order to avoid this problem, a manometer was installed in the sample line leading to the DuPont instrument, and flows from the different gas sources (either standard gas or sample port) were adjusted for constant pressure and not necessarily constant flow rate.

The discussion above and other problems concerning the instruments were worked out with the assistance of Mr. Robert Saltzman of DuPont who had major responsibility in the development of the Model 400 instrument. He spent a day at Tyco examining the sample system and the application of the photometer and concluded that accurate analysis of the various process streams would be very much dependent on sampling technique. He indicated that most of the problems he had experienced in the past were not due to machine malfunction but to problems in either sampling technique or sample stream contamination.

The problem of contamination is a very real one in the system under discussion because of the chemical species involved. The Model 400 Ultraviolet Photometer measures SO_2 concentration by attenuation of the energy at 302 mμ. NO_2, which is monitored at 436 mμ, also absorbs at 302 mμ but to a lesser extent. Great care must therefore be taken to properly balance the machine which has the capability to zero out the NO_2 influence when measuring SO_2. In addition, the nitrosyl group absorbs very strongly at 302 mμ and any deposition of nitrosylsulfuric acid on the windows of the UV cell would cause large errors in the measurement of SO_2 in the gas in the cell. Contamination on the cell windows can be zeroed out of the measurement, but if there is a continuous buildup of the material there would be a continually changing interference which would make the analytical results of marginal value.

The way to avoid interference of this sort is to maintain high temperatures in the cell and in the sample lines. If nothing is permitted to condense prior to the cold trap, there should be no problem with interference. It was felt that the gas phase constituents of $HNSO_5$ would have no effect on the readings since the nitrosyl group apparently breaks down to nitrogen oxides which can be accounted for. There is the possibility that sulfuric acid mist might absorb nitrogen oxides to form nitrosylsulfuric acid, but if the temperatures are kept high enough, this effect would be minimal. In actual operation, it was found that at temperatures below 250 °F there was a slow, continuous deposition of $HNSO_5$-bearing acid on the quartz windows of the sample cell, but as the temperature was raised this problem disappeared.

The overall evaluation of the analytical instrumentation was that they are very dependable machines and give good results as long as the sampling system was very carefully controlled. It is important to know at all times the exact nature of the sample entering the cell: its residence time in various stages of the miniplant and sampling system, its temperature, how much material might have deposited out of the gas between the miniplant and the analytical cell and any other change in condition.

3. Equipment performance

The first week of miniplant operation was on an 8-hr day basis in order to evaluate the instrumentation and the plant equipment. Without introducing any reactive components to the gas or acid streams, the various stages of the plant were run to examine their operating characteristics under process conditions.

The acid loop was started up with acid circulating at about 0.1 gpm at room temperature. Pumps, flowmeters and valves were operated and watched for a period of time, as were the scrubber and stripper columns. All phases of the acid system worked satisfactorily at low temperatures. Acid distribution throughout the columns was adequate and the pumps operated properly. However, when the system was heated up and run for a while, some intermittent problems became apparent.

The major problem in the acid system which caused several days delay in the preliminary and operating phases of the miniplant evaluation period was pump malfunction as a result of seizure of the ball check valves. By observation of the acid flowmeters it was possible to know when the pumps stopped working properly. With piston pumps such as were being used, the function of the check valves is to permit acid to be pulled into the pump from the source during the suction stroke and not allow the acid to be pulled back in from the discharge side of the pump. Conversely, on the discharge stroke, the ball check valves should shut the suction side of the pump so that the acid is pumped out of the discharge side of the pump. It was found that corrosion had caused the balls to wedge in the valves so that the check valve on the discharge side of the pump would stay open during the suction stroke with the result that the acid was pulled back into the pump from the delivery pipe. To correct this problem, all the check valves were disassembled and modified so that the balls would not stick in the valves. There were no further problems with the pumps after this was done, but unfortunately several days were lost before the problem was corrected and eliminated satisfactorily.

A less serious problem arose after the acid loop had been operated for several days. Several of the valves in the system were large stop cocks which required a lubricant to permit easy operation. After being used several times, it was found that the acid species in the gas and liquid loops were dissolving the lubricant causing the stop cock to stick. In some cases, the valve became frozen and had to be heated up to free it. All types of lubricants were used to remedy the problem including both silicone and fluorocarbon greases, but the problem continued. The only way that was found to avoid the problem was to service the valves regularly before they froze. In the future, this type of valve will be avoided and either Teflon or glass valves will be used. Saunders-Grinnell glass lined valves are used in the acid pump bypass lines as control valves and also as shutoff valves to isolate the pumps, and they are working quite satisfactorily.

The blower performed satisfactorily throughout the miniplant operating period although for 2 days flow decreased intermittently. It was found that the oil level of the blower had dropped very low. This was regularly checked thereafter, with no further problems noted.

Overall, the physical performance of the miniplant was very satisfactory and by the end of the 3-week operating period it was operating smoothly. Some modifications will be necessary for future work because of required expansion of operating characteristics, and increased flexibility, but the operating capabilities of the plant are sufficient for further optimization studies.

4. Process evaluation – initial studies

Using the start-up procedure shown in Appendix III, the 2-week period of round-the-clock operations was begun with a 12-hr interval during which the acid and gas loops were slowly brought up to operating temperatures and fluid flow rates and kept there for several hours. This was done to make sure the equipment was continuing to function properly before the reactive gases were introduced into the system.

It was during these early experiments that most of the pump problems occurred and it wasn't until late in the first week that useful operating data could be obtained. Typical results during initial reactor evaluation tests are shown in Table XIV. The SO_2 oxidation yield of 89.2% is quite satisfactory and although the NO_x balance was not as accurate as had been desired, it was still in reasonable agreement.

Continued experimentation was performed in the miniplant which evaluated both the scrubber and the stripper in conjunction with the reactor. After several days of integrated operation, a pattern seemed to develop which demonstrated the following performance levels:

SO_2 removal efficiency	75-95%
Scrubber efficiency	10-30%
Stripper efficiency	40%

Although the SO_2 oxidation reaction appeared to be satisfactory (although somewhat erratic), the scrubber and stripper were both performing below the capacity observed during the extensive laboratory testing. (It should be noted here again that all performance data obtained during the miniplant experimentation were based on the DuPont and Beckman spectrophotometers unless otherwise noted.) It was therefore decided to modify the experimental approach and concentrate on one process stage at a time, in order to determine its operating characteristics and find out the reason for the unusually poor performance of the scrubber and the stripper.

Table XIV. Miniplant Experimentation —— Reactor Evaluation*

Input gas concentration (into reactor) †

SO_2	3700 ppm ‡
NO_2	6000 ppm
NO	3000 ppm

Output gas concentration (from reactor)

SO_2	400 ppm
NO_2	3200 ppm
NO	5000 ppm

Reactor residence time	2.2 sec
SO_2 oxidation efficiency	$[(3700 - 400)/3700] \times 100 = 89.2\%$
NO_x material balance loss	$[(9000 - 8200)/9000] \times 100 = 8.9\%$

Notes:

* Gas flow rate: 8 SCFM
Reactor temperature: 300-320°F
Reactor volume = 0.5 ft^3

† All gas concentrations measured as volume ppm on DuPont and Beckman spectrophotometers.

‡ Input gases measured as fed individually to the reactor.

5. Miniplant evaluation – reactor testing

A series of runs were made in the miniplant to evaluate the performance of the SO_2 oxidation reactor. The gas was fed to the reactor from the blower using the gas burner to add water to the stream. SO_2 was fed from a cylinder and NO_2 was introduced by oxidizing NO with air in the NO oxidizer chamber. The effluent from the reactor was sent through the bypass to the stack after a sidestream was removed for analytical purposes. In other words, the reactor was run identically to the way the integrated plant was to run except that the reactor effluent was vented rather than being fed to the scrubber.

Results of several of the runs are shown in Table XV. Again the SO_2 removal efficiency is quite high, in the 75 to 95% range although the NO_x material balance was somewhat erratic. One general observation that can be made was that the change in SO_2 was not exactly equal to the reduction in NO_2 and the increase in NO. One of the difficulties was that the NO was not completely oxidized in the NO oxidizer, although it had sufficient residence time in this chamber according to the data of Burdick.[22] Another problem is that in the low temperature runs the NO probably had an opportunity to oxidize in the reactor and possibly in the sample lines. In general, it can be noted that the data show less NO and more NO_2 in the effluent than would be expected. This observation is in keeping with the idea that some of the NO was oxidized before it was analyzed.

In connection with the analytical equipment, it should be remembered that for a period of time the gas passes through a cold trap that has a fairly large residence volume. Thus the NO could be oxidized before it reaches the Beckman spectrophotometer and would therefore not be detected at all. For example, if oxidation occurred in the cold trap, the NO in the DuPont analyzer would not be detected and would be NO_2 in the Beckman and again would not be measured. This would show up as an overall shortage of NO_x , which is what has been observed.

The significant point of these data is that the experimental setup consistently gave high SO_2 removal rates under a variety of conditions. The apparent NO_2/NO ratios in the effluent gas from the reactor were in the range of 0.60 to 1.93 (see Table XV) and thus deviate from the desired ratio of 1.0. This was due to the way in which the NO_2 was prepared. There does not seem to be any reason why it cannot be controlled under more representative operating conditions. During this work, no effort was made to maintain this control except in terms of scrubber operation, which will be discussed later. In the experiments concerning reactor evaluation, control of the nitrogen oxide ratio was not emphasized.

6. Miniplant evaluation – high temperature scrubber tests

The experimental results discussed above indicated that the SO_2 oxidation reactor was apparently operating to give satisfactory removal efficiencies. If this were true and the NO_2/NO ratios in the gas entering the scrubber were as given in Table XV, then the scrubber should have been removing large percentages of the NO_x in the reacted flue gas. The scrubber efficiencies observed during some of these tests were in the 10 to 30% range, much lower than expected. Table XVI shows typical data during one of this scrubber evaluation runs. The SO_2 removal efficiency was 69 to 87% and the NO_x feed to the scrubber showed an NO_2/NO ratio in the range of 1.2 to 2.2. Perfect scrubbing of such gas mixtures on a 1:1 basis of NO_2/NO would have shown absorption efficiencies of 60 to 90%. The fact that the observed efficiencies were 6 to 18% indicates that either the scrubber was not working very efficiency (and thereby contradicting a large amount of laboratory scrubbing data) or the input gas to the scrubber was not accurately analyzed.

Table XV. Miniplant Reactor Experiments

	1	2	3	4	5	6	7	8
Reactor gas flow rate, SCFM*	9	7	7	7	5	5	8.2	9.0
Reactor residence time, sec	2.6	2.5	2.7	2.7	4.5	3.5	2.1	1.9
Reactor temperature, °F	100	324	180	182	120	320	300	290
SO_2 input concentration, ppm	2930	3200	3500	3740	4150	3350	3950	3350
NO_2 input concentration, ppm	6000	5000	6000	6000	5900	4500	7750	5100
NO input concentration, ppm	3000	3000	3000	3000	2150	2100	1500	2950
SO_2 output concentration, ppm	100	300	150	150	550	500	250	550
NO_2 output concentration, ppm	1800	†	†	1700	5600	4400	4950	3900
NO output concentration, ppm	2750	†	†	2850	2900	3175	2400	1400
SO_2 removed, %	96.7	90.6	95.7	96.1	90.6	85.0	93.6	83.6
NO_x material balance, % ‡	−50	†	†	−50	-5.6	-14.8	−20.5	−34.2
Effluent NO_2/NO ratio	0.66	—	—	0.60	1.93	1.39	2.06	2.79

---

* Air plus burner gas.

† Output NO_x data not available.

‡ Minus sign (−) indicates a loss in the NO_x output, a plus sign (+) indicates a gain.

Table XVI. Miniplant Evaluation of Scrubber*
(Wet Feed: $NO_x + SO_2$)

	Reactor** Effluent, ppm				Scrubber Effluent, ppm			
Time, min	NO	NO_2	SO_2	NO_2/NO ratio	NO	NO_2	SO_2	NO_x Scrubbing, %†
0	3850	4800	950	1.25	—	—	—	—
10	3225	4300	550	1.33	—	—	—	—
15	—	—	—	—	3000	4100	325	5.7
70	2500	4000	400	1.6	—	—	—	—
115	2325	5100	500	2.2	—	—	—	—
135	—	—	—	—	1900	4400	525	15.2
150	—	—	—	—	2000	4100	550	17.8

Notes:

* Scrubber conditions

Gas flow rate = 5 SCFM
Acid flow rate = .12 gpm
Scrubber temperature = 250°F
3/8-in. Intalox saddles
Packing height = 8.5 ft
Column diameter = 4 in

** Reactor feed: SO_2 – 3050
NO – 3500
NO_2 – 6000

† $$\%\ NO_x\ \text{scrubbing} = \frac{\text{ppm } NO_x \text{ (reactor effluent)} - \text{ppm } NO_x \text{ (scrubber effluent)}}{\text{ppm } NO_x \text{ (reactor effluent)}} \times 100$$

Additional runs were made to ascertain the low scrubbing rate and the results of one test is shown in Table XXI. The scrubbing efficiency was 8 to 9% although the SO_2 removal efficiency was about 85% and the NO_2/NO ratios was 2.2. A scrubbing efficiency of about 60% was possible on a 1:1 absorption basis. It should be noted that an NO_x material balance around the scrubber closed within 15% indicating that the analysis was not greatly in error.

The results of tests like those shown in Tables XVI and XVII suggested that there was a significant difference between the laboratory scrubbing tests and those performed in the miniplant. Examination of the operating conditions in both sets of tests show that, in addition to some differences in apparatus and temperature control, a major change that was initiated in the miniplant was the use of the SO_2 oxidation reaction products rather than an artificially prepared mixture of nitrogen oxides in a nitrogen carrier gas. Thus the gas that was fed to the laboratory scrubber was inert in the sense that it could not undergo further internal reaction. On the other hand, the scrubber feed in the miniplant was undergoing a continuing reaction between SO_2 and NO_2. The significance of this was not apparent until some tests were run in the miniplant that approximated the laboratory runs.

A miniplant experiment was conducted where the scrubber feed consisted only of moist gas containing partly oxidized NO. This was the same gas as was used in the reactor tests except that no SO_2 was introduced into the gas stream. Analysis was performed in the usual manner by sampling the effluent gases from the reactor and the scrubber and feeding them to the DuPont and Beckman spectrophotometers. Acid samples were taken from both the scrubber and the stripper so that a complete NO_x material balance could be made around the scrubber.

The results of this first test are shown in Table XVIII and indicate that the scrubber was now working at 60-65% efficiency with the feed gas containing the oxides of nitrogen in a nearly 1:1 ratio. The NO_x material balance around the scrubber closed within 4% indicating a good agreement of the acid and gas analytical techniques. (It can be noted here that the stripper is not completely denitrating the scrubber effluent acid. This will be discussed in detail in a later section of the report.) The significance of this test is that the scrubber continued to operate at relatively high efficiency (compared to the earlier runs) as long as the feed acid was low in $HNSO_5$, which tended to verify the concept that a scrubber could remove equimolar NO and NO_2 with high temperature sulfuric acid.

Another run was made in the miniplant with conditions essentially the same as in the run shown in Table XVIII. The results of this second run are shown in Table XIX and again demonstrate a high degree of scrubbing as long as the acid feed to the scrubber is low in oxides of nitrogen. As shown graphically in Fig. 37 the scrubber efficiency went down as the NO_x content in the acid feed increased. The reason for this is the theoretical limitation whereby the acid cannot reduce the NO_x concentration of the gas below that equal to the equilibrium vapor pressure over the incoming acid. Since this is true, as long as the feed acid contains a significant amount of NO_x there must be some NO_x in the scrubber effluent gas regardless of the height of the column. Because of this, the true efficiency of the column is obtained during the early stages of the

Table XVII. Miniplant Scrubber Evaluation (Wet Feed: $NO_x + SO_2$)*

Time, min	Scrubber Acid Concentration		Stripper Acid Concentration		Scrubber Effluent Gas Concentration, ppm				NO_x Scrubbing
	% H_2SO_4	% $HNSO_5$	% H_2SO_4	% $HNSO_5$	NO	NO_2	SO_2	NO_x	
				Feed:	2100	4500	500	6600	–
0	78.20	0.086	–	–	–	–	–	–	–
5	78.02	0.205	–	–	2400	3700	650	6100	7.6
10	78.02	0.194	–	–	2400	3700	–	6100	7.6
15	73.02	0.194	78.55	0.074	2400	3600	650	6000	9.1
30	78.02	0.197	78.02	0.108	2400	3600	700	6000†	9.1
45‡	–	–	78.02	0.124	–	–	–	–	–
60‡	–	–	78.20	0.088	–	–	–	–	–
90‡	–	–	78.20	0.051	–	–	–	–	–

Notes

* Gas flow = 5 SCFM
Acid flow = .12 gpm
Scrubber temperature = 250 to 265°F
3/8-in. Intalox saddles, 8.5 ft high
4-in. diameter column
Reactor input SO_2 = 3.300 ppm SO_2

† Material balance error around scrubber was 14.9%

‡ Stripping only: no NO_x fed to scrubber.

Table XVIII. Miniplant Scrubber Evaluation
(Wet Feed: NO_x only)

Time, min	Scrubber Acid Concentration		Stripper Acid Concentration		Scrubber Effluent Gas Concentration, ppm			NO_x Scrubbing, %
	% H_2SO_4	% $HNSO_5$	% H_2SO_4	% $HNSO_5$	NO	NO_2	NO_x	
				Feed:	3700	3300	7000	—
0	80.74	0.019	—	—	—	—	—	—
5	80.36	0.268	—	—	1800	700	2500	64.3
10	80.36	0.316	—	—	1775	650	2423	65.3
15	80.36	0.324	80.36	0.026	1750	650	2400*	65.7
20	—	—	—	—	1750	700	2450	65.0
25	—	—	—	—	1750	675	2425	65.3
30	80.36	0.379	80.36	0.179	1725	750	2475	64.6
40	—	—	—	—	1750	825	2575	63.2
45	80.00	0.490	80.00	0.253	—	—	—	—
50	—	—	—	—	1750	950	2700	61.4
60	80.00	0.673	80.00	0.390	1775	1100	2875†	58.8
75‡	—	—	80.00	0.435	—	—	—	—
90	—	—	80.00	0.409	—	—	—	—

Notes:

* NO_x material balance error around scrubber was 3.7%.
† NO material balance error around scrubber was 3.3%.
‡ Stripping only: no NO_x fed to scrubber.

Gas flow rate = 5 SCFM
Acid flow rate = .12 gpm
Scrubber temperature = 230 - 250°F
3/8-in. Intalox saddles, 8.5 ft high

Table XIX. Miniplant Scrubber Evaluation
(Wet Feed: NO_x only)

Time, min	Scrubber Acid Concentration		Stripper Acid Concentration		Scrubber Effluent Gas Concentration, ppm			Scrubber Temperature, °F	NO_x Scrubbing, %
	% H_2SO_4	% $HNSO_5$	% H_2SO_4	% $HNSO_5$	NO	NO_2	NO_x		
				Feed:	3425	2500	5925	248	—
0	79.8	0.085	—	—	—	—	—	—	—
5	78.9	0.330	—	—	1350	750	2160	252	64.6
10	78.7	0.323	—	—	1350	800	2150	255	63.8
15	78.9	0.330	—	—	1350	900	2250[*]	254	62.8
20	—	—	79.4	0.148	—	—	—	—	—
30	79.4	0.403	78.9	0.211	1400	1100	2500	248	57.8
35	—	—	—	—	1400	950	2350	246	60.4
40	—	—	—	—	1425	900	2325	—	60.7
45	79.1	0.453	78.9	0.281	1450	900	2350	247	60.4
50	—	—	—	—	1500	850	2350	—	60.4
60	76.5	0.498	78.7	0.352	1550	800	2350	247	60.4
75	78.7	0.527	—	—	1675	850	2525	—	57.3
90	78.2	0.543	78.6	0.419	1775	1000	2775	253	53.3
105	78.4	0.573	78.6	0.442	1850	1100	2950[†]	—	50.4
120	78.0	0.557	78.4	0.457	2000	1200	3200	—	46.2
135	77.9	0.557	78.2	0.473	2100	1450	3550	242	40.3
150	77.7	0.581	77.9	0.476	—	—	—	278	—
180[‡]	77.3	0.555	77.7	0.483	3425	1400	4825	—	18.7
195	—	—	—	—	3500	1475	4975	289	16.3
210	77.0	0.553	77.3	0.456	2650	1900	4550	—	23.3
225	—	—	—	—	2850	2050	4900	—	17.4
240	76.8	0.520	77.2	0.448	2950	2050	5000[§]	289	15.7

Notes:

[*] NO_x material balance error around the scrubber was 9.2%.

[†] NO_x material balance error around the scrubber was 5.6%.

[‡] SO_2 introduced at the 165 min mark and kept flowing at about 750 ppm concentration until the 195 min point.

[§] NO_x material balance error around the scrubber was 0.4%.

Stripper temperature 220 - 270°F.

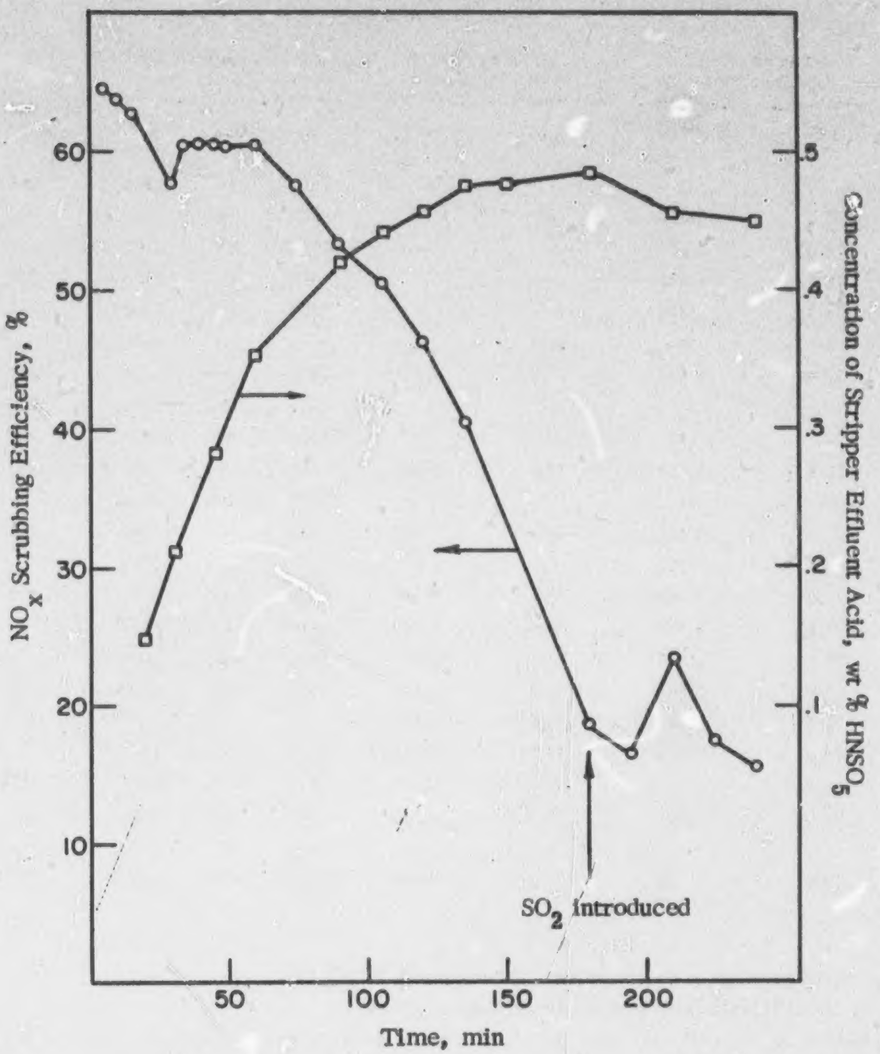


Fig. 37. Miniplant scrubber evaluation
wet feed: NO_x only
(data from Table XIX)

run when the feed acid is relatively pure. This will not be a problem when the stripper is properly operating so as to completely denitrate the acid (see part 10 of this section for a discussion of stripper operation).

The last two tests indicate that there is a difference between scrubbing the products of the reactor and scrubbing pure NO_x. Since the analysis shows the same range of NO_2/NO feed ratios as in the scrubbing tests exhibiting low efficiency, it was hard to understand the reason for the large difference in scrubbing efficiency. These tests led to a complete evaluation of what is actually occurring in the gas stream and the relationship between the miniplant system and the gas analysis system.

7. System evaluation

It is tempting to dismiss some of the anomalous results quoted above as being due to either experimental or analytical error, but the consistancy and reproducibility of the results coupled with good material balances around the scrubber verify the data. The question was: what was the difference between the scrubber experiments NO_x alone was fed to the scrubber and the tests where a mixture of NO_x and SO_2 was passed into the system?

Careful examination of the data led to the conclusion that the real difference between the two sets of tests was that in one case an inert gas was being fed to the system (inert in the sense that little or no reaction was occurring in the gas phase as it passed through the system), and in the other case a continually reacting gas was in the lines. In addition, it was concluded that the sample lines and the ultraviolet analysis cell had become part of the reaction system and the analyses made did not truly reflect the concentration of the gases in the miniplant. Instead the analyses showed the makeup of a gas stream that had undergone further reaction since it had been in the miniplant and thus the effluent and feed streams were not as had been recorded.

If these two conclusions are correct, then the scrubber data can be explained. The SO_2 was mixed with NO_x and fed to the reactor chamber where the oxidation of the SO_2 began. The gas stream was then split, with the bulk of the gas going to the scrubber and the rest, a very tiny fraction, was sent to the sample lines and photometers for analysis. As it passed through the hot sample line and into the UV cell, the gases continued to react. When the instruments finally reported the concentrations of the oxides of nitrogen and sulfur dioxide, the composition of the gas was considerably different from that entering the scrubber. The SO_2 reported was lower than that entering the scrubber as was the NO_2, while the NO observed on the Beckman instrument was probably much more concentrated than in the scrubber feed gas.

The residence times of the gas in the various parts of the system were calculated. Volumes of different parts of the system and the residence times at specific gas flow rates are shown in Table XX. It is clear that the gas passed through the sample system much more slowly than it should have. It turned out that this was due to an improperly calibrated rotameter which gave actual flows of 3.75 ℓ/min (0.13 cfm) when 1.0 cfm was expected. The bulk of the samples were taken at about 1.0 ℓ/min which gave the residence times as shown in the table.

Table XX. Residence Volumes and Times in Miniplant Reactor and Analytical System

System Phase	Residence Volume ft^3	Gas Flow Rated at STP	Residence Time, sec*
SO_2 oxidation reactor	0.4143	10 CFM	1.7
		5 CFM	3.4
		2.5 CFM	6.8
Sample lines between reactor gas effluent and UV cell	0.0041	1.0 CFM	0.2
		1.0 ℓ/min	4.9
		3.75 ℓ/min	1.3
UV cell	0.0153	1.0 CFM	0.9†
		1.0 ℓ/min	26.1
		3.75 ℓ/min	7.0

Notes

*Calculated at 300 °F

†See text for discussion of effective cell residence times.

In the determination of the total residence time, it should be realized that if there is a reaction occurring in the UV cell, the concentration of any reacting species can be roughly approximated as the linear average of the incoming concentration and the effluent concentration. The residence time of this average gas sample is therefore estimated to be one-half the total residence time of the gas in the cell. Thus, for the majority of the experiments, the effective gas residence times were 3.4 sec in the miniplant reactor, 4.9 sec in the sample lines and 13.1 sec in the UV cell.

Using these residence times, it is clear that the reason for the poor scrubbing efficiencies when the reactive mixture was fed to the scrubber was that the SO_2 had not yet been fully oxidized and there was a very large excess of NO_2 entering the scrubber. Although the laboratory data indicated that high scrubbing efficiencies could be achieved without a perfect 1:1 ratio of nitrogen oxides, the feed stream to the scrubber in the miniplant experimentation was probably excessively strong in NO_2 and thus hindered absorption. (It should also be noted that the laboratory experiments that showed good adsorption of NO_x despite an absence of the 1:1 ratio of nitrogen oxides usually had an excess of NO, not NO_2).

A significant point in the experimentation is that the high temperature scrubber worked relatively well in absorbing oxides of nitrogen when the scrubber feed gas was known to contain close to a 1:1 ratio of NO_2 and NO when SO_2 was not present.

The analysis that has just been discussed has a significant effect on the earlier analysis of the reactor. It was assumed from the reactor evaluation experimentation that the SO_2 had been almost completely oxidized in the 2 to 3 sec of residence time in the miniplant reactor.

Some experimental evidence of the oxidation of SO_2 in the sample lines was obtained by withdrawing the sample of the reactor effluent gas at varying sample line flow rates. At a flow rate of 1 ℓ/min (17 sec total residence time), about 90 to 95% of the SO_2 was removed from the gas stream. At a sample line flow of 4 ℓ/min, and a total residence time of 7.9 sec, about 30 to 40% of the SO_2 was oxidized.

A resummation of the miniplant reactor data of Table XX is presented in Table XXI showing actual residence time and reaction rate constants. Clearly, it has taken residence times in order of 20-23 sec to achieve 84-97% SO_2 oxidation. This is about four times the residence times estimated based on the experimentation performed during the previous contract (No. PH-86-68-75).

As in the previous report, the rate constants are based on the overall reaction:

$$NO_2 + SO_2 \xrightarrow[H_2O]{} SO_3 + NO$$

using the general equation

$$\frac{dx}{dt} = K\,(a - x)\;(b - x)$$

where

x = decrease in each concentration in mm Hg after time t, sec

a = initial SO_2 concentration in mm Hg

b = initial NO_2 concentration in mm Hg

K = rate constant

This can be integrated using the boundary condition that x = 0 when t = 0, and solved:

$$K = \frac{2.303}{t(a - b)}\,\log\frac{b(a - x)}{a(b - x)}$$

Table XXL Miniplant Reactor Experiments

	1	2	3	4	5	6	7	8
Reactor gas flow rate, SCFM	9	7	7	7	5	5	8.2	9.0
Reactor residence time, sec	2.8	2.5	2.7	2.7	4.5	3.5	2.1	1.9
Sample gas flow rate, ℓ/min	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sample line residence time, sec	18	18	18	18	18	18	18	18
Total residence time, sec	20.8	20.5	20.7	20.7	22.5	21.5	20.1	19.9
Reactor temperature, °F	100	324	180	182	120	320	300	290
Input concentration, ppm								
a. SO_2	2430	3200	3500	3740	4150	3350	3950	3350
b. NO_2	6000	5000	6000	6000	5900	4500	7750	5100
c. NO	3000	3000	3000	3000	2150	2100	1500	2950
d. NO_2/SO_2	2.47	1.56	1.71	1.60	1.42	1.34	1.46	1.52
Output concentration SO_2, ppm	100	300	150	150	550	500	250	550
SO_2 removed, %	96.7	90.6	95.7	96.1	90.6	85.0	93.6	83.6
Reaction rate constant, K*	0.071	0.066	0.073	0.081	0.053	0.058	0.045	0.048

---

*Units of mm, sec, °F. Note: K based on given input gas concentrations and output SO_2 removal efficiency.

Rate constants (K) from 0.045 to 0.081 have been obtained in the present effort. The calculated rate constant (K) for 90% reaction with 3000 ppm SO_2 and 6000 ppm NO_2 in sec^{-1} is 0.150. Rate constants of 0.200 were obtained in the kinetic studies of the previous work and covered a range from 0.004 in early batch studies to 0.250 under a variety of conditions. The primary difference between the present effort and the past effort is in the method of analysis and sampling, with continuous methods being used only in this study. It is anticipated that present residence times can be improved through further investigation of the reaction mechanism and optimization. However, no indication is available at this writing whether the reaction times and rates can be improved by a factor of 3-4. Thus longer residence times may have to be provided in the reactor section.

8. Scrubber design calculations

Operation of the miniplant scrubber was intended to both verify the concept of the high temperature scrubber and provide preliminary design data for process scaleup. Experimentation was designed so that calculations could be made at the conclusion of the current contract for the overall design of the scrubber. Engineering design data to be developed was to include: (1) mass transfer coefficients ($K_g a$), (2) height of a transfer unit (HTU), (3) number of transfer units (N_t), and (4) overall height of the scrubber column (Z).

The initial approach to the engineering design of the scrubber was to develop the theoretical number of transfer units needed by the use of a McCabe-Thiele analysis. Fig. 38 shows the graphical determination of 4.31 theoretical transfer units. It should be noted that this analysis is based on an assumed L/G of 4.6 moles of 80% H_2SO_4 per mole of dry gas, which was developed by a optimization cost study of the process by TVA under contract to OAP. In performing the graphical analysis, a 50% equivalent tray efficiency was assumed. The equilibrium data was obtained from the extensive work of Berl and Saenger[5] as discussed in Section V of this report (see Table XXII for a tabulation of the values for 80% H_2SO_4 nitrose solutions at 250°F).

This approach to the development of the number of transfer units was verified using a more basic approach. Treybal[23] presents an equation for the calculation of this value:

$$N_{tOG} = \frac{\ln\left[\left(\frac{y_1 - mx_2}{y_2 - mx_2}\right)\left(1 - \frac{1}{A}\right) + \frac{1}{A}\right]}{1 - (1/A)} \qquad (1)$$

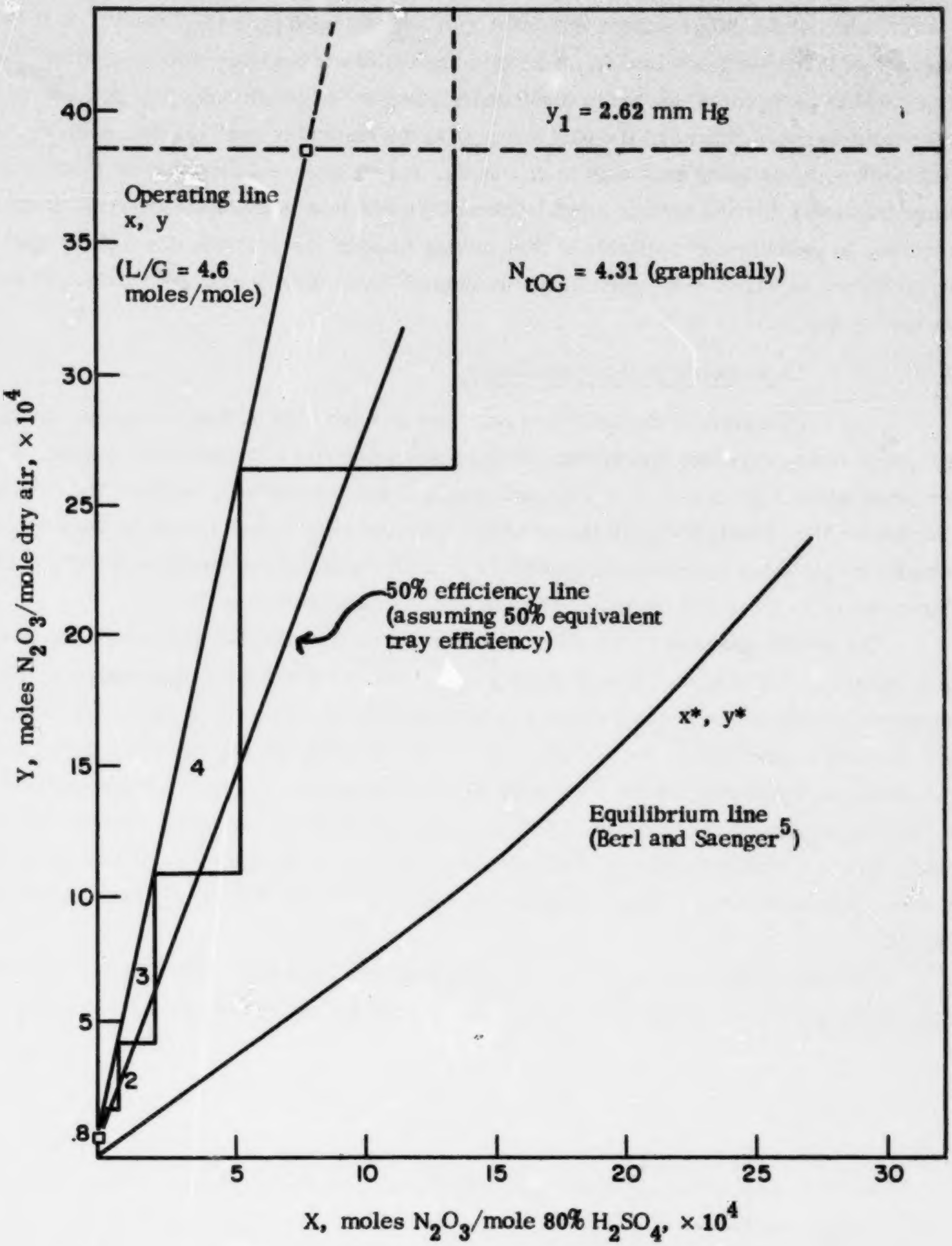


Fig. 38. McCable-Thiele analysis of high temperature scrubber

Table XXII. Equilibrium Data*

Total Vapor Pressure, mm Hg	N_2O_3 Vapor** Pressure, mm Hg	y, moles N_2O_3/mole dry air × 10^4	g-moles $HNSO_5$ per ℓ H_2SO_4	x, moles N_2O_3/g-mole 80% H_2SO_4 × 10^4
50.73	0	0	0	0
51.16	0.22	3.1	0.025	3.98
51.60	0.44	6.2	0.050	7.95
52.03	0.65	9.2	0.075	11.93
52.47	0.85	12.3	0.100	15.90
52.99	1.13	16.0	0.125	19.88
53.52	1.40	19.8	0.150	23.86
54.00	1.67	23.6	0.175	27.83
54.67	1.97	27.8	0.200	31.80
55.93	2.60	36.8	0.250	39.76

Notes:

*Experimental data of Berl and Saenger[5] at 250°F, 80% H_2SO_4

**Total vapor pressure less the vapor pressure of H_2O (50.73 mm Hg).

where

N_{tOG} = overall number of transfer units, gas

A = absorption factor = L/mG (dimensionless)

x = concentration of solute in liquid, mole fraction

y = concentration of solute in dry gas, mole fraction

m = slope of equilibrium line (dimensionless)

ℓn = natural logarithm

L = total liquid rate, lb moles/hr-ft^2

G = total dry gas rate, lb moles/hr-ft^2

The value of N_{tOG} was calculated using the following values:

L/G = 4.6 mole/mole

m = 0.77

A = 6.0

y_1 = 37.2 moles N_2O_3/mole dry gas

y_2 = 0.8 moles N_2O_3/mole dry gas

x_2 = 0 moles N_2O_3/mole dry gas

The feed and effluent gas concentrations, y_1 and y_2, were obtained from a material balance around the scrubber based on an SO_2 input of 3000 ppm. The L/G value came from the TVA optimization, and the assumption was made that the inlet acid concentration (x_2) was negligibly low. (If the stripper denitrates the nitrose at a 99% efficiency, this assumption is easily justified.) The calculation from equation (1) gave a value of N_{tOG} of 4.42 which is in very good agreement with the 4.31 obtained graphically from the McCabe-Thiele analysis.

With these values as background, experimentation was performed to determine working values for the engineering design data needed for process scaleup. The experimental runs shown in Table XVIII was used in calculation design data, but it was necessary to evaluate the scrubber at various packing depths to verify the scrubbing efficiency obtained by one height of packing. The miniplant scrubber was modified so that only 5 ft of the total 8.5 ft of packing was used for countercurrent contact between the gas and the acid. The column was fed with a mixture of nitrogen oxides as shown in Table XXIII and analyses of the gas and liquid effluents were taken as in previous tests.

Table XXIII. Miniplant Scrubber Evaluation (Wet Feed: NO_x only in flue gas; 5-ft bed height)

	Effluent Scrubber Acid Concentration		Effluent Stripper Acid Concentration		Scrubber Effluent Gas Concentration			
Time, min	%H_2SO_4	%$HNSO_5$	%H_2SO_4	%$HNSO_5$	NO	NO_2	NO_x	NO_x* Scrubbing, %
				Scrubber Feed:	3325	2950	6175	–
0	79.08	0.007	–	–	–	–	–	–
5	79.08	0.221	–	–	2150	1200	3350	45.6
10	79.08	0.229	–	–	2250	1250	3500	43.4
15	78.73	0.239	78.73	0.026	2150	1250	3400	44.8
30	78.73	0.261	78.73	0.147	2200	1200	3400	44.8
35	–	–	–	–	2250	1350	3600	41.6
45	78.73	0.320	78.73	0.173	2325	1550	3875	37.3
60**	–	–	78.73	0.202	–	–	–	–

Notes:

*L/G = 2.4 mole/mole (5 SCFM gas, .12 gpm acid)

**Stripping only: No NO_x fed to scrubber.

The analysis of scrubber operation showed that 5 ft of packed columns was capable of removing 37-47% of the NO_x in the feed gas as long as the input acid was relatively free of nitrogen oxides. The tests shown in Table XVIII show that an 8.5 ft of packed column can remove 59-66% of the NO_x under the same operating conditions.

These two data points can be used to analyze the performance of taller columns. If 5 ft of packing can remove 45% of the NO_x then the next 5 ft can remove 45% of the remainder for a total of 70%. This can be expanded for greater packing heights as shown in Table XXIV. The same treatment can be performed on the other set of data and this is also shown in Table XXIV. Both sets of data are plotted in Fig. 39 and are mutually consistent since they both fall on the same efficiency curve. Examination of this curve shows that 97% scrubbing efficiency can be achieved with about 30 ft of packed column, certainly a reasonable packing height. (99% scrubbing could be achieved with 35 to 40 ft of packing).

Table XXIV. Extrapolated Scrubbing Efficiencies Based on Experimental Column Tests

Column Height, ft	% NO_x Removed	Column Height, ft	% NO_x Removed
5	45*	8.5	65*
10	70	17	88
15	83	25.5	96
20	91	34	99
25	95		
30	97		
35	98		

---

*Experimental data obtained in the absence of SO_2 is the scrubber gas.

The height of a transfer unit can be obtained from the curve in Fig. 39 by making a simplifying assumption. This assumption is developed by Sherwood and Pigford[24] by examination of the following definite integral which is used for the estimation of tower parameters:

$$N_{tOG} = \int_{y_2}^{y_1} \frac{dy}{y - y_e} \qquad (2)$$

where

N_{tOG} = overall number of transfer units, gas

y = gas phase concentration of solute

y_e = gas phase concentration when at equilibrium with the liquid phase.

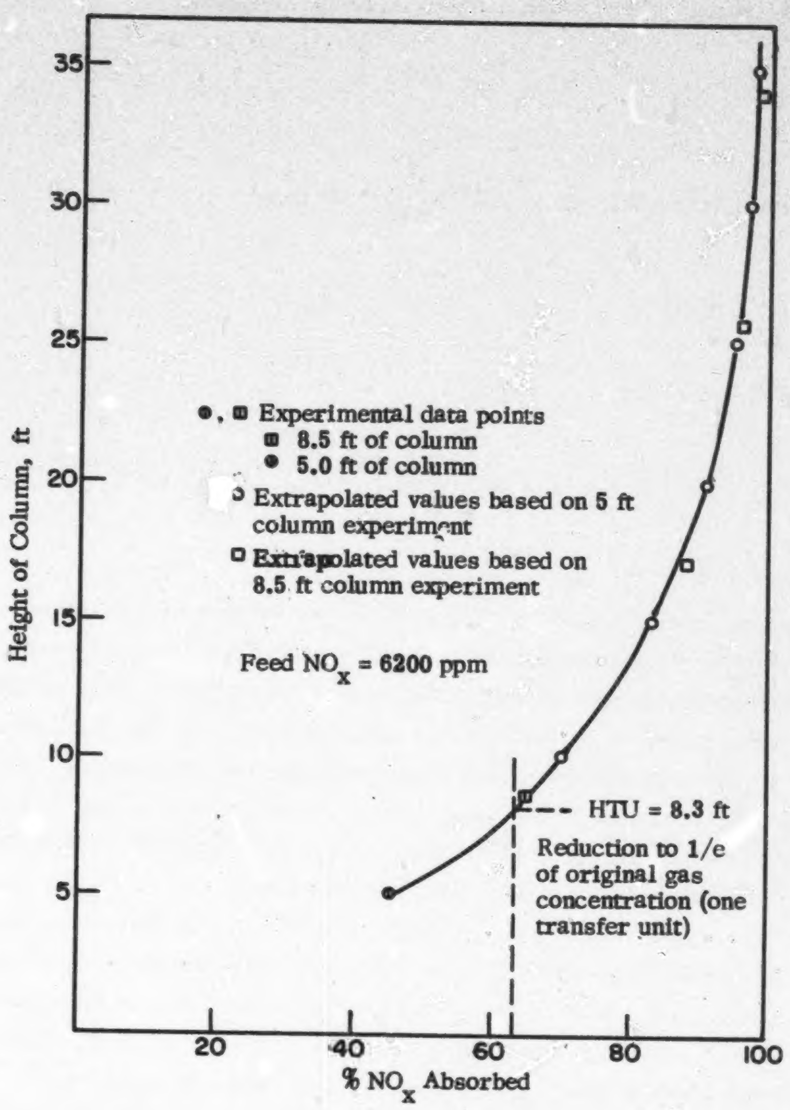


Fig. 39. Scrubbing efficiency of packed column; experimental and extrapolated values used to determine HTU

The simplifying assumption is that if the vapor pressure of the solute over the liquid is very low compared to the concentration of the solute in the gas being scrubbed, then y_e is small enough to be ignored. The equation can then be easily integrated:

$$N_{tOG} = \ell n \frac{y_1}{y_2}$$

If one transfer unit is being considered $(N_{tOG} = 1)$, then:

$$\ell n \frac{y_1}{y_2} = 1 \tag{3}$$

and

$$\frac{y_1}{y_2} = e \tag{4}$$

This means that, if the assumed conditions pertain to the system in question, one transfer unit will reduced the outlet gas concentration to 1/e (or 37%) of the feed composition.

In examining this approach with respect to the N_2O_3/H_2SO_4 system existing in the scrubber, it can be shown that the vapor pressure of N_2O_3 over the dilute nitrose solutions existing in the system is relatively low compared to the gas composition. Typically the vapor pressure would be about 15-20% of the gas phase concentration (see Fig. 38 for a comparison of the operating line with the equilibrium line). This is not a negligible value, but it is low enough to allow the use of the technique for a first approximation.

To determine the HTU by this method, the curve in Fig. 39 is examined and the column height is read at 63% scrubbing efficiency. As shown on the graph, one HTU is equal to 8.3 ft of packed column. The actual number of transfer units could then be determined by dividing the height needed to obtain 99% scrubbing (35-40 ft) by the HTU (8.3 ft). This gives a value of N_{tOG} of 4.2-4.8 which is fairly close to the predicted values of 4.3 to 4.4.

The determination of HTU can be done more rigorously using the experimental data in Treybal's simplified equation for the determination of number of transfer units in a dilute gas system in conjunction with equations for mass transfer coefficient, $K_y a$, and height of a transfer unit, HTU[23]

$$N_{tOG} = \frac{y_1 - y_2}{(y - y^*)_M} \tag{5}$$

where

$$(y - y^*)_M = \frac{(y - y^*)_1 - (y - y^*)_2}{\ln (y - y^*)_1/(y - y^*)_2} \qquad (6)$$

y_1 = feed gas concentration, mole fraction

y_2 = effluent gas concentration, mole fraction

y^* = equilibrium vapor pressure of solute over acid in contact with scrubber gas of concentration y

Thus $(y - y^*)$ is the vertical distance between the operating line and the equilibrium line. The other equations are:

$$G(y_1 - y_2) = K_g a\ Z\ P_t\ (y - y^*)_M \qquad (7)$$

or, from equation (5):

$$K_g a = \frac{G\ N_{tOG}}{Z\ P_t} \qquad (8)$$

where

$K_g a$ = overall mass transfer coefficient, gas, lb-moles/hr - ft^3 - atm

G = gas flow rate, moles/hr - ft^2

P_t = total pressure, atm.

Z = height of packing, ft.

and

$$HTU = \frac{Z}{N_t} \qquad (9)$$

where N_t here refers to the number of transfer units in a column with Z ft of packing.

The equilibrium data from Table XXII is plotted again in Fig. 40 with the operating line for an L/G of 4.6 plotted for reference. In addition, the experimentally determined operating lines for the tests shown in Tables XVIII and XXIII are plotted on the same graph. The values

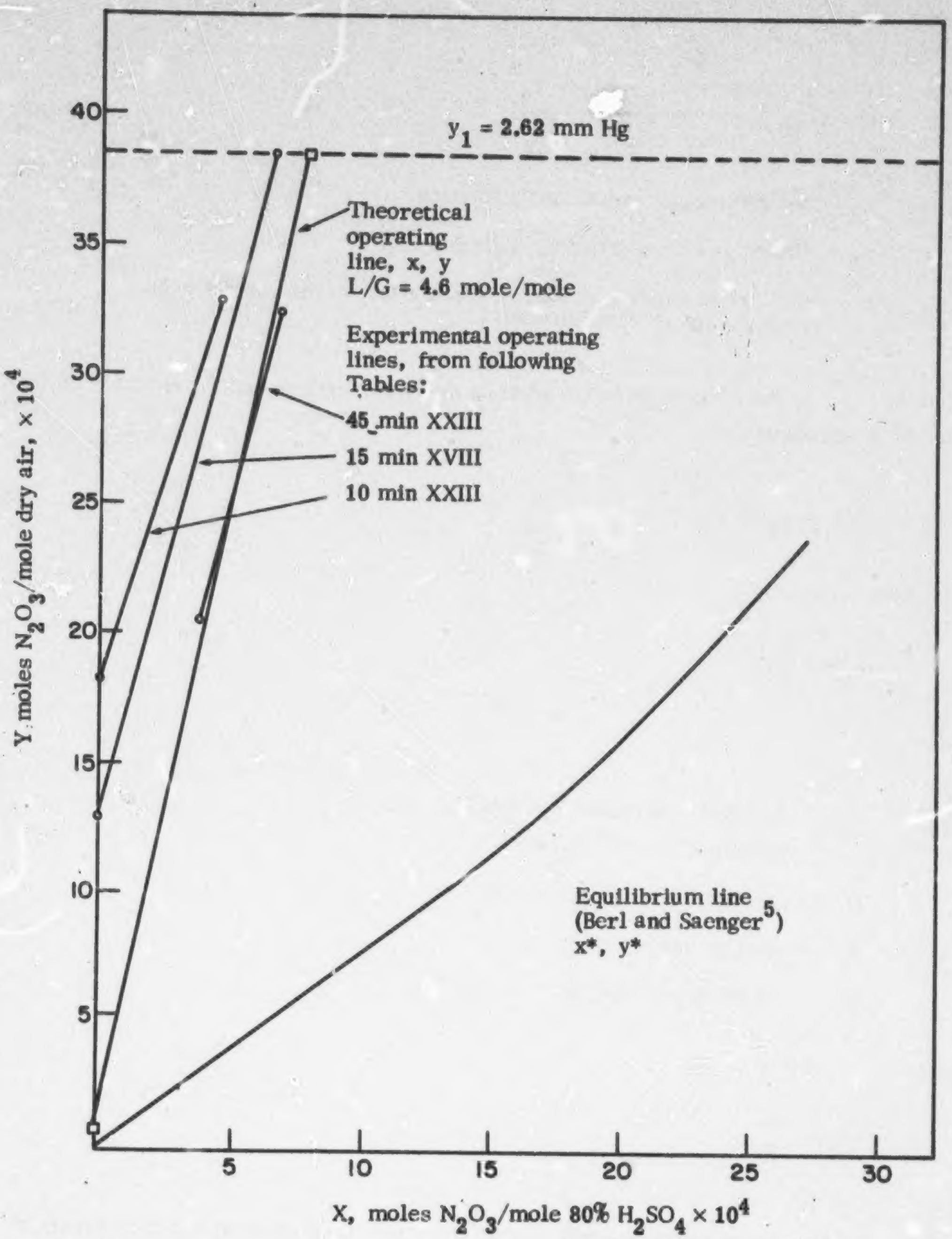


Fig. 40. Experimental operating lines – scrubber design

of $(y - y^*)$ are taken as the vertical distances between these experimental operating lines and the equilibrium line and are used in equation (5) to determine experimental values of N_t. It should be remembered that in this case N_t is the number of transfer units in the given column to effect the absorption shown by the experimental operating line and is not the total number of transfer units needed to achieve the desired 99% absorption of NO_x. This was done for the three cases chosen for analysis.

The values of N_t were then used to calculate the mass transfer coefficients using equation (8). HTU values were determined using the values of N_t in equation (9). All calculated results are shown in Table XXV and are compared to the values obtained by the simplified analysis of the data using the curve in Fig. 39.

What is significant about these data is the close agreement of the calculated values with each other and with the simplified analysis. Although the values of HTU are somewhat higher than usually encountered in industrial practice, the number of these units needed to effect the desired absorption is relatively low as shown by the calculated values of N_{tOG} in Table XXIX. It is also interesting to note that these values of N_{tOG} are quite close to the predicted values of 4.3 and 4.4 determined by McCabe-Thiele graphical analysis and mathematical computation.

The values of mass transfer coefficient, height of transfer unit, and number of overall transfer units obtained experimentally by operation of the miniplant will be invaluable in future work. Both plant scale-up and future miniplant operation will be aided by the development of these figures. The values are not the final ones since considerably more experimentation will be performed to refine figures, but they certainly present the order of magnitude of these vital parameters. It should be noted here again that there was no SO_2 present during these NO_x absorption experiments.

Table XXV. Calculation of Mass Transfer Coefficients ($K_g a$) and Height of Transfer Unit (HTU)*

Reference	z, Packed Height, ft	N_t†	$K_g a$‡	HTU, ft
Table XVIII	8.5	1.16	1.31	7.4
Table XXIII (10 min)	5	0.61	1.17	8.3
Table XXIII (45 min)	5	0.55	1.06	9.1
Fig. 39	–	1	1.17	8.3
Averages	–	–	1.18	8.3

---

*In these experiments the following conditions pertained: G = 9.59 moles gas/hr-ft^2; Z is given for each test above; P_t = 1 atm total pressure.

†N_t refers to the number of transfer units in the packed height shown in the table.

‡moles/hr-ft^3-atm.

9. Water balance in scrubber

One of the key features of the high temperature scrubber was its capability of scrubbing NO_x from the reacted flue gas while maintaining the concentration of the recycle acid. Examination of the miniplant operating data shows that this capability was demonstrated in several runs. The tests described in Tables XVII and XVIII show good water balance maintenance in both the scrubber and the stripper loops. In the test shown in Table XIX, there was a slow decrease in acid concentration indicating that water was being absorbed, causing dilution. This test shows the need for proper temperature control in the system, not only in the scrubber itself, but also in the acid feed. Although the scrubber temperature was maintained near 250 °F throughout the test, the input acid was cooler and thus caused absorption of water at the top of the column. In general, the data clearly show that the concept of scrubbing at high temperatures to avoid water absorption is feasible.

10. Stripper evaluation

A tabulation of stripper results during simultaneous operation of the scrubber, as presented in Tables XVII, XVIII, XIX, and XXIII are graphically represented in Figs. 41, 42, 43, and 44. Fig. 43 is the most meaningful as the stripper-scrubber operation was performed over a prolonged time period.

In these figures, starting time zero indicates the time scrubber operation is begun. Approximately 10 min are required at a flow rate of 0.16 gal/min to obtain a sample at the bottom of the stripper, due primarily to residence in the feed line. The accumulated stripper data with time is thus indicative of conditions occurring in the scrubber ten minutes earlier. Furthermore, the stripper bottoms are collected in a reservoir of approximately 5 gal hold capacity while being continuously refed to the scrubber. Thus, where partial stripping is achieved (as in the case of these data), the rate of nitrosylsulfuric acid buildup in the scrubber acid feed is retarded as a result of dilution in the reservoir. Both of these factors are evident in the initial shapes of the curves presented.

Two pertinent conclusions can be drawn from the data presented:

1. The present miniplant stripper design cannot denitrate at a rate fast enough to maintain integrated operation without modification.

2. Despite the buildup of nitrosylsulfuric acid, some denitration was obtained. As can be noted from the relatively parallel stripper-scrubber curve in Fig. 43, denitration at steady state appears to occur in the stripper at an essentially constant rate.

In view of the extremely encouraging earlier laboratory data on the stripper, a reassessment of thescale-updesign conditions in the miniplant stripper was made. With limited available laboratory design and optimization data, the miniplant stripper was sized for a similar L/G ratio and roughly comparable residence times in the packed bed. No change was made in the type or size of charcoal catalyst used. It was hoped that satisfactory stripping could be achieved at considerably higher space velocities than obtained in laboratory equipment. A comparison of the

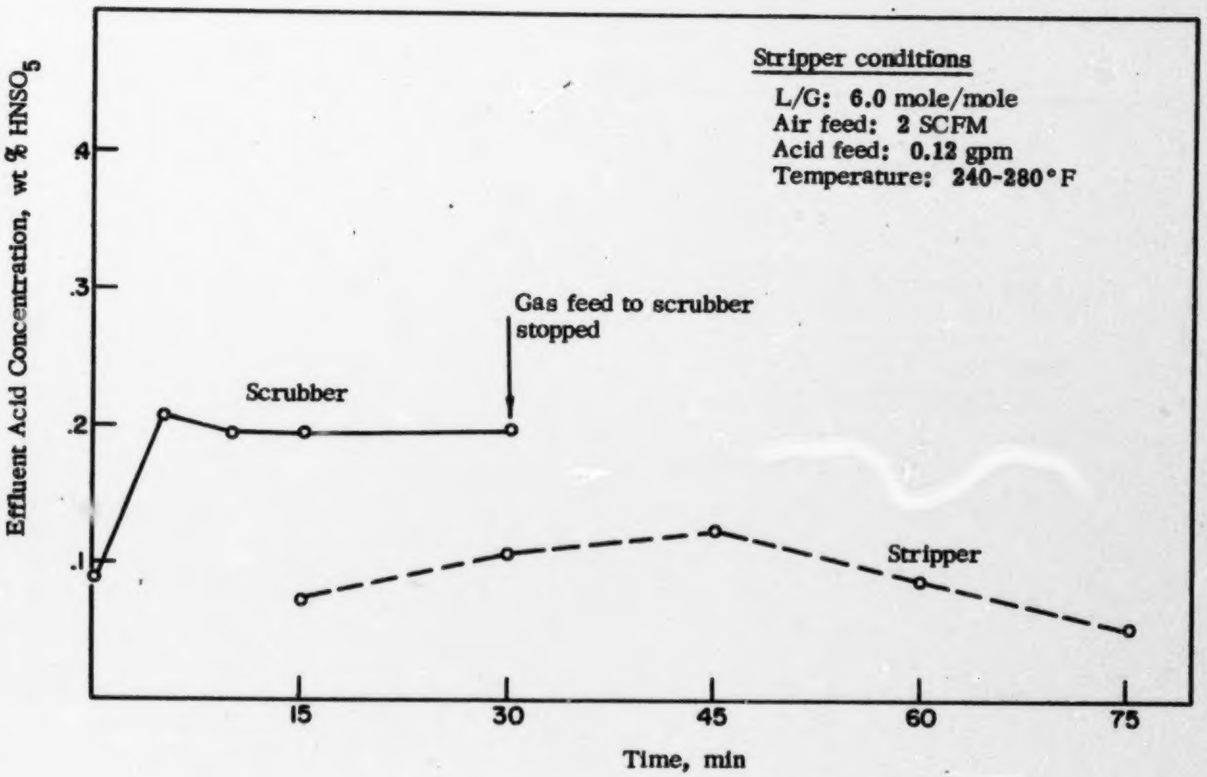


Fig. 41. Scrubber/stripper operation in miniplant - data from Table XVII

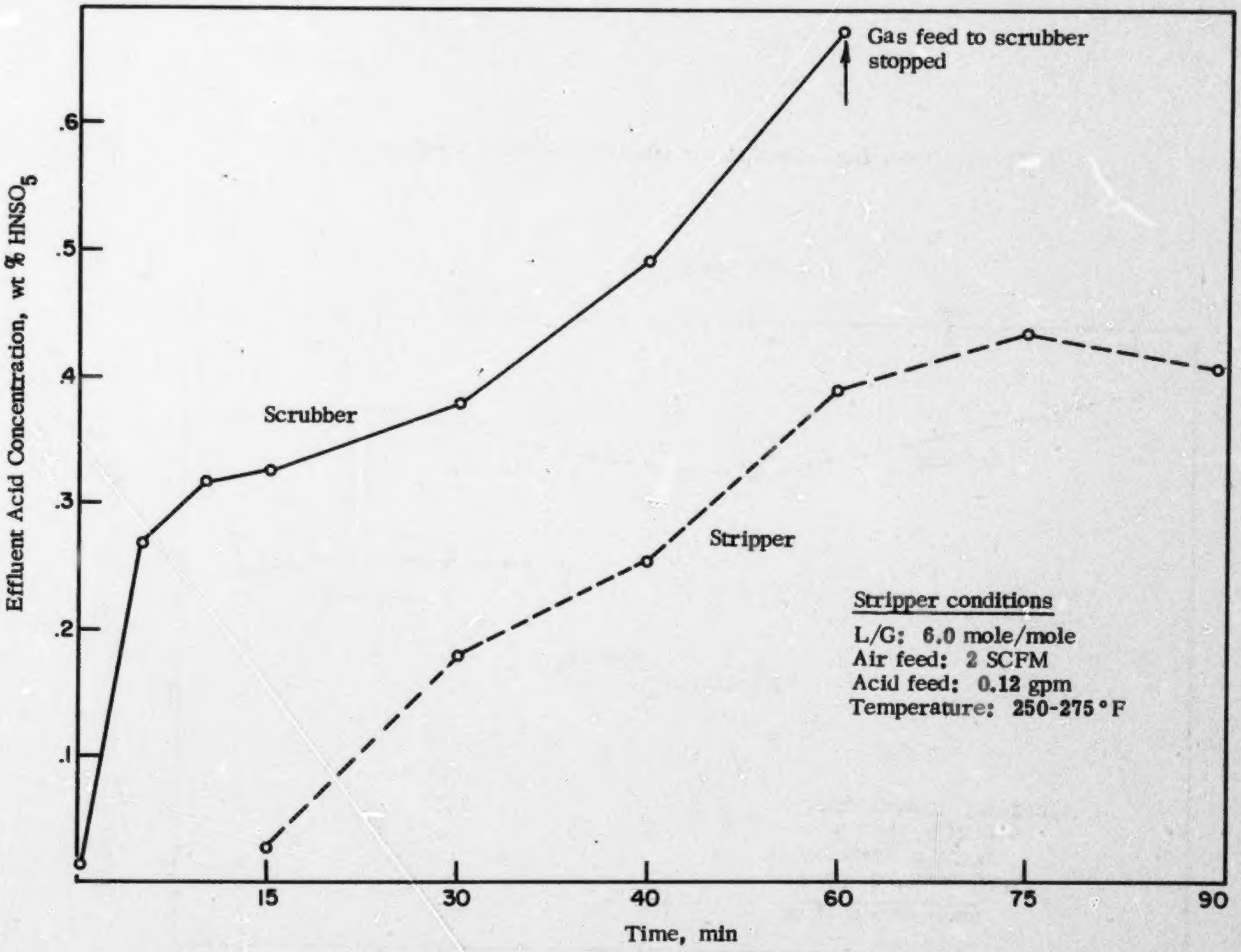


Fig. 42. Scrubber/stripper operation in miniplant - data from Table XVIII

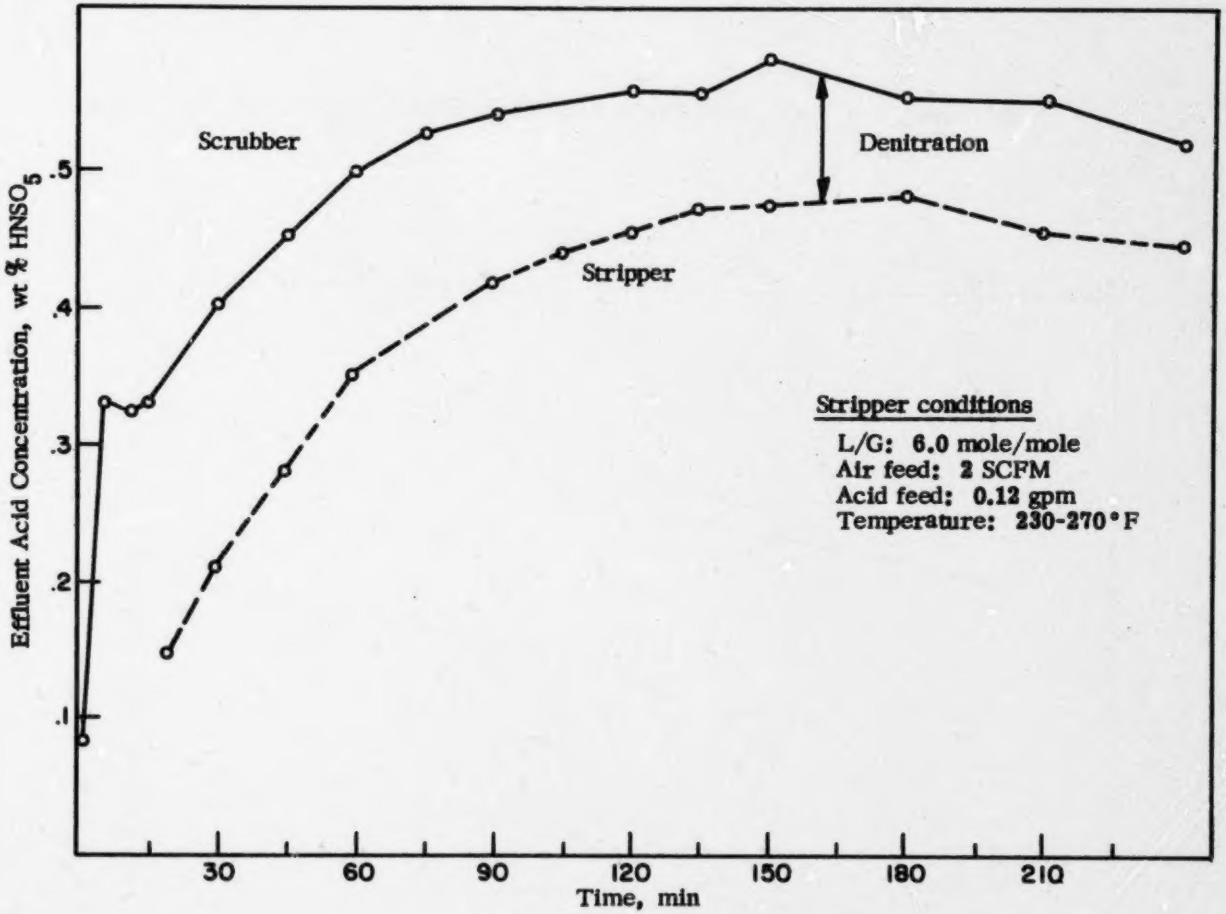


Fig. 43. Scrubber/stripper operation in miniplant - data from Table XIX

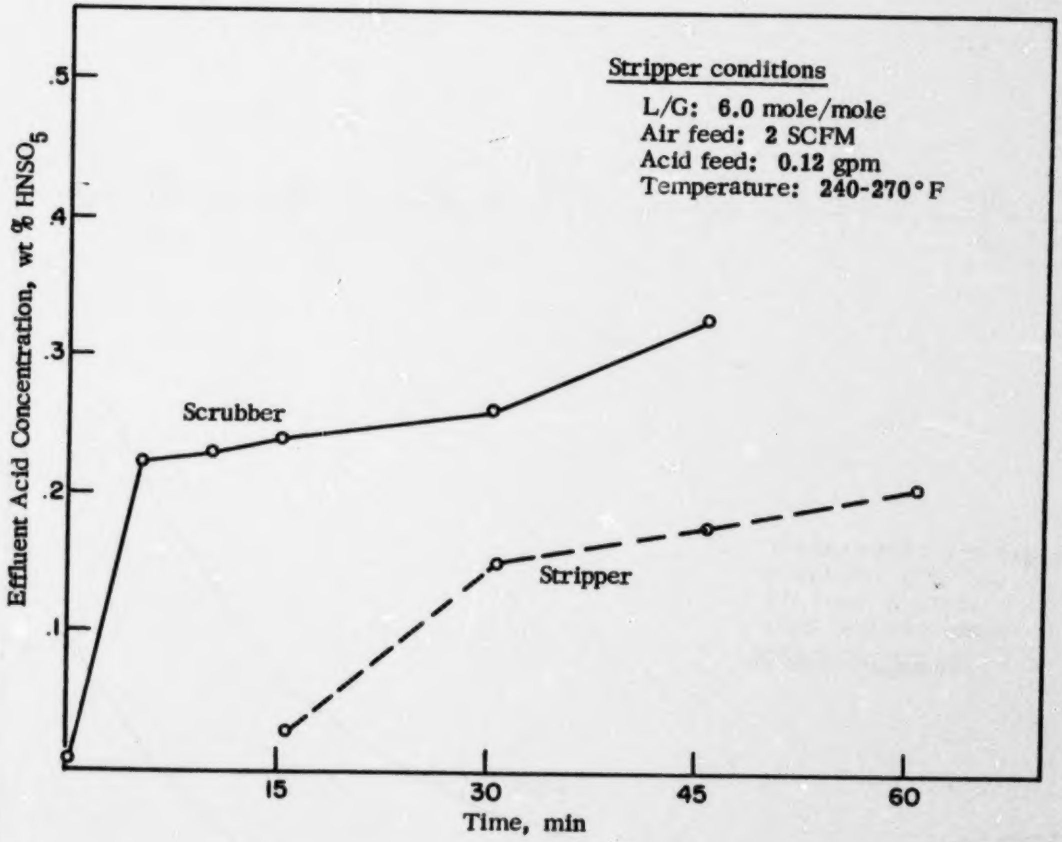


Fig. 44. Scrubber/stripper operation in miniplant - data from Table XXIII

conditions in the laboratory and miniplant catalytic strippers are presented in Table XXVI. The conditions used in later experiments are also noted in the table.

Table XXVI. Design and Conditions for Operation of Laboratory and Miniplant Catalytic Stripper

		Miniplant		
	Lab	Initial Design	Verification Experiments	
			1	2
I Column				
Diameter of column, cm	5.08	10.16	10.16	10.16
Height of catalyst bed, cm	25.4	81.2	81.2	81.2
Volume of catalyst bed, mℓ	510	6580	6580	6580
II Flow				
(L) Acid flow rate, g/min	17.3	1,310	65	104
(G) Gas flow rate, g/min	1.08	97	6.15	6.15
L/G mole/mole	9.3	7.8	6.2	9.8
III Space Velocity(Liquid),				
Volume of acid, ℓ per hr per volume of catalyst	1.18	12.0	0.34	0.54

As noted by Johnstone and Thring,[25] the overall rates of many heterogeneous chemical reactions are controlled by the rates at which the reacting substances are brought together or products removed at the interface. Apart from such dynamic factors, the rate of a heterogeneous chemical reaction is influenced by the interfacial area between the phases, the extent to which reactants and products are absorbed at the interface, and the specific catalytic activity the interface may possess. The reaction velocity is normally represented by a generalized equation of the form:

$$U = -\frac{da}{dt} = \phi\,[\,K_n F(a,\ a_2 \ldots a_n)\ \alpha s]$$

where:

U = reaction rate, expressed as moles of reactant A which react per unit volume and time

a = concentration of reactant A per unit volume

t = time

ϕ = function

K_n = a velocity constant for a reaction of the nth order

F = a dimensionless kinetic factor derived from the activity coefficients of the reactants and products

$a_1 a_2 \ldots a_n$ = molar concentrations of reactants $A_1 A_2 \ldots A_n$, respectively

α = a dimensionless factor proportional to the catalytic activity of the surface or interface

s = specific surface or interface per unit volume.

For the general case in which the overall linear dimensions and specific surface are independent of one another, the generalized equation becomes:

$$\frac{K_n F (a_2 \ldots a_n)\, \alpha\, s \mathcal{L}}{v} = \phi \left(\frac{q a_1}{C_p \rho T}, \frac{q a_1 v}{H_w} \right)$$

where

q = heat of reaction per mole

C_p = specific heat at constant pressure

ρ = density

T = temperature

v = linear velocity of reaction mixture

H_w = heat loss per unit area of wall in unit time

$\mathcal{L}$ = linear dimension

In the case of an identical catalyst for both lab model and pilot plant, there is a particular advantage of having the bed heights identical. Thus units α, s, $\mathcal{L}$ and v are fixed, and a close approach to similarity can be obtained (similar space velocities, similar linear velocites) provided that surface heat losses per unit volume and time can be controlled. Preliminary calculations have indicated that the heat generated in the stripper would heat the system only one or two degrees, and thus can be neglected at this stage of scale-up. The similarity of space velocities remain to be verified.

Two experiments were made to test the aforementioned approach in the miniplant stripper, recognizing that no change in the catalyst or catalyst height would be made in the limited time available and that the conditions used in the laboratory stripper were not optimized. For these exerpiments, quantities of unstripped nitrose solution were accumulated during scrubber operation and retained without going through the stripper. The nitrose solutions were subsequently fed to the stripper (scrubber and scrubber lines operating only as a means of heating the retained solution to operating temperatures) at reduced liquid and air flow rates simulating the L/G and space velocities used in the laboratory reactor. These conditions are noted in Table XXVI and the results presented in Tables XXVII and XXVIII.

As can be seen from the data of the two experiments, average nitrosylsulfuric acid stripping efficiencies averaged 99% + for Experiment 1 and 95% for Experiment 2. Excellent total material balance agreement was obtained in the second run where more suitable liquid flow and temperature control was maintained. Although of limited operating duration, the material balance agreement of the second run provides considerable credibility to the data obtained. Visual examination of the catalyst after the experimentation showed no particulate deterioration even though the catalyst had been subjected to greater than 200 hr of operation.

Although the operating conditions of the stripper have not yet been optimized, examination of the data in Tables XXVII and XXVIII suggests two disquieting factors which may influence future work on the stripper:

1. Significant quantities of NO (averaging 20 to 34% by volume of the total NO_x removed from the acid) were present in the effluent gas.

2. The concentration of NO_x in the exit gas averaged 1.1 to 2.0% by volume.

Analysis of the data makes it apparent that catalytic denitration of the nitrose solutions did occur. If the stripper in the experiment described in Table XXVII were denitrating the acid only by thermal decomposition of the nitrosylsulfuric acid, the maximum concentration of N_2O_3 in the effluent gas would be given by the equilibrium vapor pressure. Under the conditions of this experiment, this would be equivalent to about 8500 ppm of N_2O_3 or 17000 ppm of total NO_x. In the second experiment (Table XXXII), the equilibrium vapor pressure would have been about 4500 ppm of N_2O_3 or 9000 ppm of NO_x. In both cases, the amount of NO_x given off was slightly higher than this.

It should be noted that, although the total NO_x evolved was significantly higher than the equilibrium vapor pressure, the amount of NO was consistently lower than would be expected from equilibrium considerations while the NO_2 was consistently higher. This tend to verify the contention that NO is emitted only because of its vapor pressure while the NO_2 is mainly being formed by catalytic oxidation of the nitrose.

Fig. 45 is a schematic diagram of a stripper that would effectively denitrate the nitrose and provide an effluent gas that would contain a high enough concentration of NO_2 to permit the economical production of nitric acid while containing a minimum amount of NO. This would be accomplished while conforming to the results of both the laboratory experiments and the mini-plant operation. The stripper would be operated at a lower L/G with the bulk of the gas passing through the column being recycled back to the bottom of the unit. Fresh air would be fed to the bottom of the column as in previous operation.

Table XXVII. Miniplant Stripper Verification Experiment No. 1

Time min.	Acid Pumping Rate, cc/15 min.	Air Flow, cc/min at STP	Stripper Temperature, °F			Effluent Gas, ppm		Effluent Acid		% $HNSO_5$ Denitrification
			Top	Middle	Bottom	NO	NO_2	% H_2SO_4	% $HNSO_5$	
0	–	–	–	–	–	–	–	–	0.667*	–
15	623	4732**	134	243	224	4400	12,000	84.04	0.011	98.3
30	644	4732	282	298	262	4900	24,200	82.93	0.008	98.6
45	616	4732	294	324	286	4575	23,200	82.12	0.004	99.4
60	456	4732	246	310	286	3350	12,400	82.52	0.004	99.4
75	480	4732	172	290	261	2725	9,400	81.71	0.004	99.1
Average:	–	–	–	–	–	3990	16,240	82.66	0.006	

Total acid pumped: 2819 cc

---

*Initial $HNSO_5$ Concentration

**0.167 SCFM

Table XXVIII. Miniplant Stripper Verification Experiment no. 2

Time min.	Acid Pumping Rate, cc/15 min	Air Flow, cc/min at STP	Stripper Temperature, °F			Effluent Gas, ppm		Effluent Acid	
			Top	Middle	Bottom	NO	NO_2	% H_2SO_4	% $HNSO_5$
0	–	4732**	188	282	276	–	–	78.2	0.385* 0.374* 0.374*
15	1000		194	270	268	2600	3650	78.2	0.011
30	780		245	258	258	3275	5350	78.2	0.011
45	913		268	248	242	3275	6500	78.2	0.007
60	900		275	248	236	3525	7200	78.2	0.048
75	870		290	258	240	3850	8100	78.2	0.055
90	915		296	270	250	4200	8800	78.2	0.037
105	870		292	282	260	4400	9200	78.4	0.015
120	865		294	292	282	4325	8800	78.4	0.015
135	910		295	302	296	4400	8700	78.4	0.018
150	935		290	308	312	4250	8200	78.4	0.011
165	910		291	310	320	4325	8000	78.2	0.007
180	905		290	310	320	4200	7650	78.2	0.007
Average	898	–	–	–	–	3885	7513	78.2	0.0201***

Total Acid Pumped: 10773

---

*Initial $HNSO_5$ Concentration

**0.167 SCFM

***Equivalent to 94.8% denitration

The advantages of this approach to the stripper are that the recycling of the gas stream permits the buildup of the concentration of NO_2 while operating the column at low L/G. At the same time, the concentration of NO in the effluent gas stream is limited to the equilibrium vapor pressure, and it is unlikely that the conditions at the top of the stripper would approach equilibrium. (Laboratory experience suggests that effluent concentrations would be in the range of about 50% of the equilibrium concentration.) This would mean that the gas leaving the stripper would have a composition of about 7 to 10% NO_2 and about 0.4% NO. This amount of NO could easily be accounted for in the total process system by recycling an equivalent amount of NO_2 to the reactor loop to permit total absorption of NO_x in the scrubber on a 1:1 NO_2: NO basis.

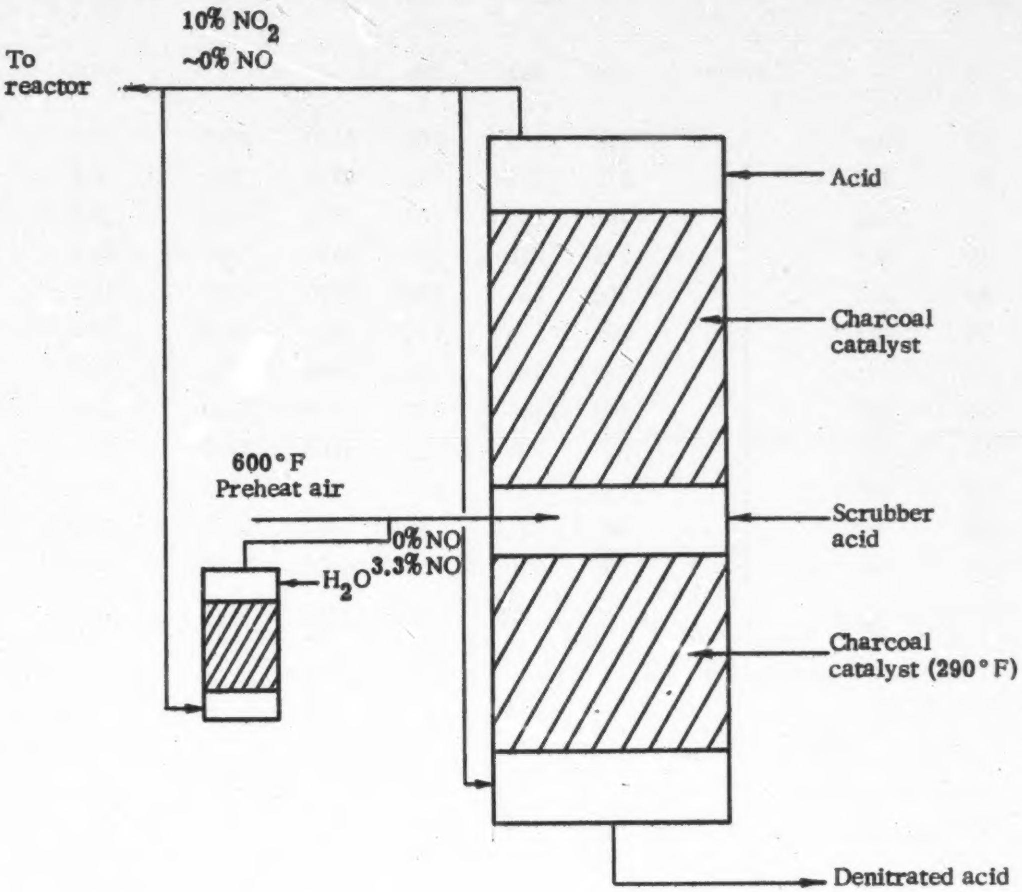

10% NO_2
~0% NO
To reactor
Acid
Charcoal catalyst
600 ° F
Preheat air
Scrubber acid
0% NO
3.3% NO
H_2O
Charcoal catalyst (290 ° F)
Denitrated acid

Fig. 45. Modified catalytic stripper - recycle concept

There is one problem that might be encountered in the operation of a stripper as shown in Fig. 45 and that is the possibility of the acid leaving the column picking up some NO_x from the concentrated gas stream entering at that point. This is somewhat unlikely because the stripper column is very short and should be very inefficient as a scrubber, but the possibility can be anticipated.

There are two approaches to this problem which would prevent the loss of NO_x and consequent contamination of the product acid. First, another short, charcoal-packed stripper section could be added at the bottom of the column shown in Fig. 45. In that section, the effluent acid would come in contact with fresh air at a very high L/G and could be effectively denitrated in the usual manner.

Another approach would be to inhibit the absorption of NO_x by reducing the amount of NO in the recycle gas stream. If the NO_x is being absorbed only in equimolar quantities of NO and NO_2, then the maximum absorption would be all the NO plus the equivalent amount of NO_2 or about 0.2% of each. To reduce this absorption, the NO concentration can be decreased by oxidizing it before it reenters the stripper. This could be accomplished by catalytic air oxidation.

There is considerable evidence in the literature that NO can be oxidized catalytically at relatively high temperatures at rates almost one thousand times greater than the homogeneous reaction. Burdick[2] shows that activated charcoal, in particular, is an excellent catalyst in the air oxidation of NO. This suggests that a way to reduce the amount of NO in the stripper recycle gas stream would be to add a catalytic oxidizer section using charcoal as the catalyst.

It is clear that more work is necessary in order to fully define the configuration and operating characteristics of the catalytic stripper. The first order of business is to determine the optimum operating conditions: temperature, L/G, space velocity, bed depth, etc. When these parameters have been optimized the stripper can be modified to produce a product gas of the proper concentration of NO and NO_2.

11. Miniplant operation conclusions

As previously noted, the miniplant effort is the result of less than 1 month of round-the-clock operation on an integrated and semi-integrated basis. All phases of the work requirements were completed. Based on the experimental work performed, the following conclusions can be drawn:

1. All systems involced in the Catalytic Chamber Process were shown to be technically feasible.

2. A 84 to 97% oxidation of SO_2 in the concentration range of 3000 ppm (0.3%) was found to occur at 300°F in approximately 20 to 23 sec. This oxidation time was somewhat higher than anticipated from previous laboratory studies.

3. Operation of the high temperature scrubber was verified and good scale-up agreement was obtained. The theoretical number of transfer units was calculated to be about 4.4, whereas extrapolation of the experimental data showed a requirement of about 3.7 units. Calculations of HTU indicated a requirement for 8.3 ft of column per transfer unit. Gas side mass transfer coefficients were calculated to be 1.18 moles/hr/ft^2/atmosphere. These data are sufficient for initial construction of a column to demonstrate the desired absorption; i.e., a 30-ft packed column to absorb 97% of the NO_x in the feed stream at L/G ratios used. The column is well within the limits of feasibility from size and material considerations. Data was obtained on gases containing no SO_2.

4. The catalytic stripper was operated and demonstrated to denitrate the scrubber acid at greater than 97% yields, as required for suitable stripper operation. Preliminary scale-up criteria for the stripper have been obtained. Denitration has been found to yield sizeable quantities of nitrogen dioxide and less than the equilibrium amount of nitric oxide.

5. On the basis of present results, it is desireable to continue to study the Catalytic Chamber Process on the current miniplant scale. Stepwise, this would entail: (1) modification of the miniplant equipment as required, (2) statistical optimization of operating and design conditions, (3) verification of commercial feasibility and (4) pilot plant design.

VII. ACKNOWLEDGEMENTS

We gratefully acknowledge the assistance of Irving Frutkoff, Mourad Ghobrial, Robert Fragala, and David Cogley in performing the experimental research and in preparing this report. We also acknowledge the advice and assistance of William Elder and Gerald McGlamery of the Tennessee Valley Authority. The contributions of Stanely Bunas of the Office of Air Programs of the Environmental Protection Agency are acknowledged with gratitude.

VIII. REFERENCES

1. A. C. Stern, "Air Pollution," Vols. 1 and 3, Academic Press, New York, 1962.
2. NAPCA Report, Sulfur Oxides Pollution Control, PB 180769, April 1968.
3. Anon., Chemical and Engineering News, July 8, 1968.
4. D. Bienstock, J. H. Field, S. Katell, and K. O. Plants, Journal of Air Pollution Control Association, 15, 459-464 (1965).
5. E. Berl and H. H. Saenger, Z. Anorg. Allgem. Chem., 202, 113-134 (1931).
6. W. F. Giaque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, J. Amer. Chem. Soc., 82, 62-70 (1960).
7. Greenwatt, Inc. Eng. Chem., 17, 522 (1925).
8. A. Hantzch and K. Berger, Chem. Ber., 63, 321-336 (1930).
9. I. E. Ioshpa and L. E. Zlotnik, J. Appl. Chem. USSR, 29, 937 (1956).
10. T. I. Kunin, J. Appl. Chem. USSR, 27, 248-57 (1954).
11. T. I. Kunin, and N. A. Sorov, J. Appl. Chem. USSR, 23, 136-139 (1950).
12. K. Malin, "The Technology of Sulfuric Acid," Moscow (1941).
13. M. Matsui, J. Soc. Chem. Ind. Japan, 30, 134 (1927).
14. W. J. Mueller, D. M. Forbes, and R. Fort, Angew. Chem., 45, 782-785 (1932).
15. A. Sanfourche and L. Rondier, Compt. Rend., 30, 815 (1928).
16. K. Stopperka and F. Kilz, Z. Anorg. Allg. Chemie, 348, 58-70 (1966).
17. L. E. Topol, K. B. Oldham and R. G. Adler, J. Inorg, Nucl. Chem., 30, 2977-90 (1968).
18. L. E. Topol, R. A. Osteryoung and J. H. Christie, J. Electrochem. Soc., 112, 861-864 (1965).
19. A. N. Tseitlin and V. T. Yavorskii, J. Appl. Chem. USSR, 39, 698-699 (1966).
20. A. N. Tseitlin and V. T. Yavorskii, J. Appl. Chem. USSR, 39, 977-981 (1966).
21. M. L. Varlamov, J. Appl. Chem. USSR, 23, 127-135 (1950).

Preceding page blank

22. C. L. Burdick, J. Amer. Chem. Soc., 44, 244 (1922).

23. R. E. Treybal, Mass-Transfer Operations, McGraw-Hill Book Co., Inc., 1955 .

24. T. K. Sherwood and R. L. Pigford, Absorption and Extraction, McGraw-Hill Book Co., Inc., 1952.

25. R. E. Johnstone and M. W. Thring, Pilot Plants, Models, and Scale-Up Methods in Chemical Engineering, McGraw-Hill Book Co., Inc., 1957.

APPENDIX I

PROCESS ECONOMICS

Table XXIX. Estimated Major Equipment Cost*

Item	Task	No.	Size	Cost
Cyclone separator	Remove coarse fly ash	3	487,000 cfm	$ 245,000
Scrubber	Remove N_2O_3, H_2SO_4, and fly ash	3	35-ft diameter 70 ft high 8 ft/sec	1,500,000
Stripper	Recover N_2O_3	2	32-ft diameter 60 ft high 2 ft/sec	250,000
NO_3 absorber	Recover NO_x at 52% HNO_3		44-ft diameter 60 ft high	450,000
Filter	Remove fly ash from acid	3		250,000
Product storage tank	Store H_2SO_4	3		100,000
Exhaust fan	Provide differential pressure	3	12 in. H_2O 87 mm SCFH	60,000
Gas cooler	Cool stripper gas	1	2.5 mm BTU/hr 2100 ft sq. area	20,000
Gas cooler	Cool reactor gas	6	124 mm BTU/hr 105,000 ft sq. area	525,000
Pumps	Move acid from scrubber to stripper	8	3800 gal/min	50,000
Pumps	Move acid from stripper to scrubber	8	3800 gal/min	50,000
				$3,500,000

---

*800 megawatt (e) power plant producing 1.44×10^6 SCFM flue gas.

Table XXX. Estimated Capital Cost Summary*

	Item	Factor
1.	Major equipment (see Table III)	1.00
2.	Erection labor and foundation	0.38
3.	Piping	0.55
4.	Instruments	0.05
5.	Insulation	0.03
6.	Electrical	0.05
7.	Building	0.20
8.	Plant facilities	0.05
9.	Plant utilities	0.08
10.	Receiving, shipping, etc.	0.05
11.	Physical plant costs	2.44
12.	Engineering and construction	0.60
13.	Direct plant cost	3.04
14.	Contractor's fee	0.10
15.	Contingency	0.15
16.	Fixed capital costs	3.29

17. Total fixed capital costs = \$3,500,000 × 3.29 = \$11,515,000

---

*800 megawatt (e) power plant producing 1.44×10^6 SCFM flue gas.

Table XXXI. Annual Operating Costs[*]

Raw materials and chemicals		
Catalyst replacement	$ 100,000	
Water (3500 GPM at $0.10/M gal)	168,000	
Direct labor	108,000	
Supervision	27,600	
Maintenance at 0.05 of fixed capital	653,000	
Supplies at 15% of maintenance	98,000	
Utilities		
Power	145,700	
Heat	0[†]	
Total direct cost		$1,300,300
Payroll burden (20% of direct labor and supervision)	16,600	
Plant overhead (50% of direct labor, supervision, maintenance, and supplies)	416,600	
Packing and shipping	425,000	
Waste disposal	25,000	
Total indirect cost		$ 873,200
Depreciation (10% of fixed capital)	$1,151,500	
Taxes (2% of fixed capital)	230,300	
Insurance (1% of fixed capital)	115,150	
Total fixed cost		$1,496,950
Total operating cost		$3,670,450 (or $1.64/ton of coal)

---

[*] 800 megawatt (e) power plant producing 1.44×10^6 SCFM flue gas.

[†] Heat is needed only for startup and process adjustment situations.

APPENDIX II

NITROSYLSULFURIC ACID ANALYSES

APPENDIX II. NITROSYLSULFURIC ACID ANALYSES

A classical wet chemical analysis method is being used to analyze the liquid effluents from the scrubber and the stripper to determine the nitrogen oxide content of the streams. Aliquots of the acid solutions are titrated with potassium permanganate (0.1M) which acts as its own indicator, to a faint pink end point which remains for at least 5 min. It may be noted that, near the end of the titration, the reactions involved proceed more slowly due to the very low concentration of $NHSO_5$ remaining. This procedure depends on the hydrolysis of the N_2O_3 to HNO_2 which is then oxidized by the permanganate to HNO_3:

$$NHSO_5 + H_2O \rightarrow H_2SO_4 + HNO_2$$

$$5\ HNO_2 + 2\ HMnO_4 \rightarrow HNO_3 + 3\ H_2O + 2\ Mn\ (NO_3)_2$$

One problem with this technique is that it will not accurately determine any excess dissolved NO_2, which is hydrolyzed to an equimolar mixture of HNO_2 and HNO_3. Since the nitric acid cannot be oxidized any further, the permanganate will not react with half of the NO_2 dissolved in the acid. (It should be emphasized that all the NO_2 associated with N_2O_3 will be determined because no HNO_3 is obtained when the N_2O_3 is hydrolyzed.) This will probably not be a significant problem since very little NO_2 should be dissolved in the acid. In any case, any discrepancy in the amount of nitrogen oxides will show up in the complete material balance around the various stages in the process. The technique has been tried several times in the laboratory and has shown good reproducibility (about 1%).

One precaution that will be necessary is to avoid very high concentrations of sulfuric acid in the analysis. Titration of 50% nitrosylsulfuric acid in 98% H_2SO_4 with 0.1 molar $KMnO_4$ resulted in the liberation of a great deal of heat which caused the nitrosylsulfuric acid to break down with the resulting evolution of brown NO_2 fumes which were lost to the analysis. When diluted with 80% sulfuric acid so that the acid and nitrogen oxide concentrations were lower (about 2% $HNSO_5$), the temperature did not rise as much during the titration and no NO_2 was lost. Care must be taken to add the permangate solution sufficiently slowly so as not to cause siginficant heating of the nitrosyl solutions. The use of a surrounding ice bath may be employed.

APPENDIX III

MINIPLANT EXPERIMENTAL PROCEDURES

APPENDIX III. MINIPLANT EXPERIMENTAL PROCEDURES

A. Miniplant Operating Concept

The goal of the miniplant operation was to start the plant, achieve steady state and then vary a few operating parameters to obtain experimental verification of the basic concept of the Catalytic Chamber Process and to obtain preliminary order-of-magnitude engineering data. Since only 2 weeks were alloted to this task, it was realized that this examination would be very limited in scope and there would be no time to go into the operation of any one particular process stage in great depth. This work was to provide initial data and would be followed up by more extensive optimization studies at a later time.

B. Startup Procedure

A startup procedure was carefully worked out so that the plant could be slowly brought to steady state operation without sudden changes occurring in the system that might be dangerous to either equipment or personnel. Since the integrated plant had never been run it was necessary that each stage of the plant be brought into operation individually for observation before the next stage of operation was started up. Table XXXII shows the startup procedure used to begin the operation of the miniplant.

Table XXXII. Miniplant Startup Procedure

1. Start blower with stack and vent by-passes open. Adjust stack by-pass to give 10 SCFM. Start air through NO oxidizer.
2. Start acid pumps for scrubber and stripper.
3. Start air through stripper. Control to desired level.
4. Turn on cooling water to condensers and gas burner.
5. Start heating system. Set all variacs at 40: reactor, scrubber, stripper and sample lines.
6. Turn on instrumentation. Allow at least 15 min warm-up for recorder. UV and IR photometers are left on at all times. For initial startup allow 2 hr warm-up for both instruments. Two hours should be allowed for trap cooling bath to reach -40°C.
7. Adjust heating levels as necessary. Raise heating by increasing variacs. Sample lines are kept on 40.
8. Turn on gas burner. Allow about 30 min to reach steady state. Readjust air flow.
9. Zero and span instruments.
10. Introduce SO_2 and NO into system.
11. Close vent bypass, sending gas flow through scrubber. Readjust all flow rates for new pressure drop condition. Readjust temperature as necessary.

C. Safety Considerations

Safety precautions were carefully followed throughout the operation of the miniplant. All personnel were equipped with protective gear which included acid resistant coveralls, rubber gloves, safety glasses, face shields, hard hats and boots. Other safety precautions that were followed included having two operators in attendance at all times, keeping lime available for acid spills, avoiding placement of tools or other objects on the apparatus where they could fall and break glass piping, and keeping a gas mask convenient at all times.

The plant was set up so that in case of an accident all the electrical equipment (heaters, pumps, blower) could be turned off remotely. A self-contained breathing apparatus was kept outside the plant area in case of a major gas leak. A large exhaust fan was installed in the area which could change the air in the room within 1 min. Although there were a few minor gas leaks and acid spills, there was never any occasion for emergency action.

D. Data-Taking Procedures

During miniplant operation, all aspects of the plant were monitored on a regular basis and operating data taken at specific intervals. This was done, not only to obtain the data for calculations and future reference, but also to provide a check list for the operators so they would be forced to observe all operating equipment at regular intervals and make sure operating levels were maintained throughout an experiment.

Forms were prepared for recording data in addition to a log book which was maintained for general comments and discussion. Copies of these forms are shown in Tables XXXII through XXXVI of Appendix IV.

APPENDIX IV

MINIPLANT DATA SHEETS

Table XXXIII

SO_2: Zero ______ Span ______

NO_2: Zero ______ Gain ______

NO: Gain ______

Date: ______

Page: ______

			NO_2			SO_2				
Condition	Time	Air Rotameter	Rotameter	ppm	No ppm	Rotameter	ppm	N_2O_3 Rotameter	Low Air Rotameter	Comments

Table XXXIV

MANOMETERS			FLOWMETERS							ACID ANALYSIS						DATE:						
										SCRUBBER			STRIPPER									
SCR.	STR	TOTAL	GAS IN	NO	AIR (NO)	AIR (STR)	ACID SCR	ACID STR	SO_2	ML		%	ML		%							

Table XXXV

TEMPERATURES

DATE:

TIME	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20

1. Hot water heater
2. Blower inlet
3. Blower outlet
4. Reactor inlet
5. Reactor
6. Reactor outlet
7. Scrubber inlet gas
8. Scrubber
9. Scrubber gas outlet
10. Scrubber acid feed (at pump)
11. Scrubber acid feed (at top)
12. Scrubber acid outlet
13. Stripper acid feed (at pump)
14. Stripper acid feed (at top)
15. Stripper - top
16. Stripper - middle
17. Stripper - bottom
18. Stripper acid reservoir
19. Stripper gas exit
20. NO oxidizer outlet

Table XXXVI

LOG AND VARIAC SETTINGS DATE:

TIME	1	2	3	4	5	6	7	8	9	10	11	12	13	14	